Supporting Information
for
"N_2 Functionalization at Iron Metallaboratranes"

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Contents

Experimental Part

General considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thoroughly sparging with Ar gas followed by passage through an activated alumina column in the solvent purification system by SG Water, USA LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. (TPB)FeBr (**1**) was synthesized as previously reported[1]. Elemental analyses were performed by Midwest Microlab, LLC., Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3-Å molecular sieves prior to use. Deuterated THF was dried over NaK alloy prior to use. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane, using residual solvent proton and ^{13}C resonances as internal

[1] Moret, M.-E.; Peters, J. C.; *Angew. Chem. Int. Ed.* **2011**, *50*, 2063-2067.

standards. ^{31}P, ^{11}B, and ^{29}Si chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4, $BF_3{\cdot}Et_2O$, and tetramethylsilane, respectively. Multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (double doublet), while apparent singlets, doublets, and triplets are indicated by "s", "d", and "t", respectively. Solution phase magnetic measurements were performed by the method of Evans.[2] IR measurements were obtained on samples prepared as KBr pellets or in dilute solution using a Bio-Rad Excalibur FTS 3000 spectrometer. X-band EPR spectra were obtained on a Bruker EMX spectrometer and simulated using Easyspin.[3] Optical spectroscopy measurements were taken on a Cary 50 UV-Vis spectrophotometer using a 1-cm two-window quartz cell.

X-Ray Crystallography. XRD studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer (Mo Kα radiation). Structures were solved using SHELXS[4] and refined against F^2 on all data by full-matrix least squares with SHELXL. The crystals were mounted on a glass fiber. Relevant details are reported in Table 1.

Computational methods. Geometry optimizations were performed using the Gaussian03 package.[5] The B3LYP exchange-correlation functional was employed with a 6-31G(d) basis set. The GDIIS

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[2] a) D. F. Evans, *J. Chem. Soc.* **1959,** 2003-2005; b) S. K. Sur, *J. Magn. Reson.* **1989,** *82,* 169-173.

[3] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*(1), 42-55.

[4] Sheldrick, G. M. *Acta. Cryst.* **2008**, *A64*, 112.

[5] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q.

algorithm was used. A full frequency calculation was performed on each structure to ensure that they are true minima. NBO [6] analyses were performed on the electron density obtained at the B3LYP/6-311+G(d,p)//6-31G(d) level.

(TPB)Fe(NNSiMe$_3$) (3). A solution of (TPB)FeBr (**1,** 30 mg, 41 μmol) in THF (2 mL) was stirred over sodium amalgam (4.5 mg, 0.2 mmol Na ; 0.9 g Hg) for 20 h. The resulting dark red solution that contains [(TPB)Fe(N_2)]Na (**2**) was decanted away from the amalgam and cooled down to ca −60 °C, and chlorotrimethylsilane (6 μL, 47 μmol) was added *via* syringe, causing an immediate color change to brown. The mixture was allowed to warm up to room temperature and stirred for 15 min before the volatiles were removed *in vacuo*. Extraction with pentane (4 × 0.5 mL) followed by concentration and drying *in vacuo* afforded the product as brown microcrystals (28 mg, 91 %). Crystals suitable for XRD were obtained by slow concentration of a pentane solution of **3** in a closed vessel containing hexamethyldisiloxane. ^{1}H NMR (C_6D_6, 300 MHz): δ 17.4 (3H), 13.6 (v br, 3H), 11.5 (3H), 6.5 (3H), 6.3 (br, 3H), 2.7 (9H), 1.3 (9H), 0.5 (3H), −1.7 (18H), −2.6 (9H). UV-Vis (DEE, nm {$cm^{-1}M^{-1}$}): 320 {sh}, 400 {sh}, 580 {sh}, 790 {140}. μ_{eff} (C_6D_6, Evans method, 20 °C): 1.7 μ_B. IR (KBr): ν_{NN}= 1741 cm^{-1}. Anal: calcd for $C_{39}H_{63}BFeN_2P_3Si$: C 62.63, H 8.50, N 3.75; found: C 61.71, H 8.45, N 3.26.

Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[6] (a) Feed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 899. (b) Weinhold, F.; Landis, C. R. Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective; Cambridge University Press: New York, 2005.

[(TPB)Fe(NNSiMe$_3$)]Na(THF) (4). *Method A.* Freshly prepared sodium amalgam (14 mg, 0.61 mmol Na; 3.2 g Hg) was added to a brown solution of (TPB)FeBr (**1,** 50 mg, 69 μmol) and trimethylsilyl chloride (12 mg, 110 μmol) in THF (3 mL) and vigorous stirring resulted in a color change to dark chocolate brown over ca 10 min. The mixture was stirred for an additional 3 h, sodium amalgam was removed by decantation and the solvent was removed *in vacuo*. The resulting brown solid was thoroughly washed with pentane (2 + 3 × 0.5 mL) and then extracted with benzene to yield a dark brown solution. Lyophilization yielded [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) as a brown powder (43 mg, 74 %). Concentration of the pentane washings afforded a small amount of (TPB)Fe(NNSiMe$_3$) (**3**) (9 mg, 17%). Crystals suitable for XRD were obtained by vapor diffusion of pentane into a benzene solution of **4**. ^{1}H NMR (C_6D_6, 300 MHz): δ 8.14 (1H, d, ^{3}J(H–H) = 7.2 Hz, Ar–H), 7.85 (1H, d, ^{3}J(H–H) = 7.3 Hz, Ar–H), 7.70 (1H, br 't', Ar–H), 7.40–7.13 (5H, m, Ar–H), 7.01 (1H 't', ^{3}J(H–H) = 6.4 Hz, Ar–H), 6.12–5.96 (2H, br m, Ar–H), 4.31 (1H, m, FeCH), 3.29 (4H, m, OCH_2), 3.10–2.70 (4H, m, PCH), 2.32–2.13 (1H, m, PCH), 2.05–1.90 (2H, m, PCH), 1.86 (3H, dd, ^{3}J(H–P) = 13.2 Hz, ^{3}J(H–H) = 6.7 Hz, CCH_3), 1.77 (3H, dd, ^{3}J(H–P) = 14.4 Hz, ^{3}J(H–H) = 6.7 Hz, CCH_3), 1.63–1.43 (9H, m, CCH_3), 1.38 (3H, dd, ^{3}J(H–P) = 8.9 Hz, ^{3}J(H–H) = 7.5 Hz, CCH_3), 1.26 (4H, m, OCH_2CH_2), 1.18–0.84 (15H, s, CCH_3), 0.25 (9H, s, $SiCH_3$), 0.04 (3H, dd, ^{3}J(H–P) = 13.7 Hz, ^{3}J(H–H) = 6.9 Hz, CCH_3). ^{31}P NMR (C_6D_6, 121 MHz): δ 105.1 (d, ^{2}J(P–P) = 42.6 Hz), 88.5 (d, ^{2}J(P–P) = 42.5 Hz), 9.1 (s). ^{11}B NMR (C_6D_6, 128 MHz): δ 21 (br). ^{13}C NMR (C_6D_6, 125 MHz): δ 146 (br, C^{Ar}), 143.8 (C^{Ar}), 139.8 (C^{Ar}), 139.5 (C^{Ar}), 132.3 (C^{Ar}), 132.1 (C^{Ar}), 131.4 (C^{Ar}), 131.2 (C^{Ar}), 127.3 (C^{Ar}), 124.1 (C^{Ar}), 123.2 (C^{Ar}), 115.7 (C^{Ar}), 111.0 (C^{Ar}), 92.3 (br, C^{Ar}), 68.04 (OCH_2), 64.0 (FeCH), 33.5 (br, PCH), 29.5 (PCH), 29.4 (PCH), 29.1 (PCH), 29.0 (PCH), 27.7 (PCH), 27.6 (PCH), 25.4 (OCH_2CH_2), 25.3 (PCH), 23.13 (PCH_3), 23.07 (PCH_3), 22.8 (PCH_3), 22.6 (PCH_3), 21.6 (PCH_3), 21.4 (PCH_3), 21.0 (PCH_3), 20.3 (PCH_3), 20.2 (m, PCH_3), 19.74 (PCH_3), 19.69 (PCH_3), 18.23 (PCH_3), 18.18 (PCH_3), 16.0 (PCH_3), 15.9 (PCH_3), 1.1 ($SiCH_3$). UV-Vis (Benzene, nm {$cm^{-1}M^{-1}$}): 310 {sh}. Anal: calcd for $C_{43}H_{71}BFeN_2NaOP_3Si$: C 61.29, H 8.49, N 3.32; found: C 60.96, H 8.34 N 3.34. *Method B.* Freshly prepared sodium amalgam (3.9 mg, 0.17 mmol Na; 1.2 g Hg) was added to a

brown solution of (TPB)Fe(NNSiMe$_3$) (**3,** 19 mg, 25 μmol) and vigorous stirring resulted in a color change to dark chocolate brown over ca 10 min. The mixture was stirred for an additional 1 h and worked up as described above to yield **4** as a brown powder (10 mg, 47 %).

(TPB)Fe(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 5). Freshly prepared sodium amalgam (48 mg, 2.09 mmol Na; 9.8 g Hg) was added to a brown solution of (TPB)FeBr (**1**, 250 mg, 0.34 mmol) and bis(chlorodimethylsilyl)ethane (82 mg, 0.38 mol) in THF (15 mL) and vigorous stirring resulted in a color change to dark green over ca 10 min. The mixture was stirred for an additional 3 h, sodium amalgam was removed by decantation and the solvent was removed *in vacuo*. The resulting dark green solid was thoroughly extracted into pentane (5 mL) to obtain a dark green solution that was slowly concentrated to ca 0.2 mL by vapor diffusion into hexamethyldisiloxane over 2 days. Decantation followed by washing with cold hexamethyldisiloxane (3 × 0.2 mL) afforded the product as a dark green, microcrystalline solid (210 mg, 75 %). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.50 (3H, d, ^{3}J(H–H) = 7.2 Hz, Ar–H), 7.10–7.00 (6H, m, Ar–H), 7.00–6.95 (3H, m, Ar–H), 2.55–2.40 (3H, m, PCH), 1.94 (3H, sept, ^{3}J(H–H) = 7 Hz, PCH), 1.50–1.39 (18H, m, CCH_3), 1.22 (9H, br dd, ^{3}J(H–P) = 12 Hz, ^{3}J(H–H) = 7 Hz, CCH_3), 0.71 (9H, br dd, ^{3}J(H–P) = 11 Hz, ^{3}J(H–H) = 7 Hz, CCH_3), 0.68–0.52 (4H, m, $SiCH_2CH_2Si$), 0.37 (6H, s, $SiCH_3$), 0.24 (6H, s, $SiCH_3$). ^{31}P NMR (C_6D_6, 121 MHz): δ 99.1. ^{11}B NMR (C_6D_6, 128 MHz): δ 27 (br). ^{29}Si NMR (C_6D_6, 99 MHz): δ 4.4. ^{13}C NMR (C_6D_6, 125 MHz): δ 167.4 (br, C^{Ar}), 145.9 (m, C^{Ar}), 131.1 (m, C^{Ar}) 129.8 (C^{Ar}), 127.4 (C^{Ar}) 123.4 (C^{Ar}), 30.9 (m, PCH), 30.0 (m, PCH), 23.2 (CCH_3), 22.9 (CCH_3), 22.2 (CCH_3), 20.6 (CCH_3), 9.1 (s, ^{1}J(C–^{29}Si) = 57 Hz, $SiCH_2CH_2Si$), 0.7 (m, $SiCH_3$), −0.9 (m, $SiCH_3$). UV-Vis (DEE, nm {$cm^{-1}M^{-1}$}): 270 {35000}, 340 {sh}, 410 {sh}, 650 {570}. Anal: calcd for $C_{42}H_{70}BFeN_2P_3Si_2$: C 61.61, H 8.62, N 3.42; found: C 61.38, H 8.59, N 2.95.

(TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 6). A dark green suspension of **5** (106 mg, 0.13 mmol) in tetramethylsilane (1 mL) was degassed by freeze-pump-thaw and stirred under one atmosphere of CO at 40 °C for 24 h. During that time, the supernatant first turned dark brown, then green when **6** started precipitating, then finally light brown when most of the starting

material was consumed. Filtration, washing with TMS (3 × 0.5 mL) and drying *in vacuo* afforded the product as a black powder (86 mg, 78 %) that gave inky burgundy solutions in benzene. ^{1}H and ^{31}P NMR indicated the presence of ca. 15% of a minor species that is tentatively assigned as an isomer of **6**. Crystals suitable for XRD were obtained by slow concentration of a tetramethylsilane solution of **6** in a closed vessel containing hexamethyldisiloxane. ^{1}H NMR (C_6D_6, 300 MHz): δ 8.25–8.11 (1H, m, Ar–H), 7.50–6.85 (11H, m, Ar–H), 3.1 (2H, br, PCH), 2.6 (1H, br, PCH), 1.9 (3H, br, PCH), 1.5 (6H, br, CCH_3), 1.24 (6H, br dd, ^{3}J(H–P) = 16 Hz, ^{3}J(H–H) = 7 Hz, CCH_3), 1.1–0.9 (18H, m, CCH_3), 0.52 (4H, s, $SiCH_2CH_2Si$), 0.2 (12H, br, $SiCH_3$). *Minor species:* δ 0.6 (4H, s, $SiCH_2$), 0.31 (12H, br, $SiCH_3$). ^{31}P NMR (C_6D_6, 121 MHz): δ 86 (br, Fe–P), 85 (br, Fe–P), 0.4 (s, unbound P). *Minor species:* δ 90.8 (br, 2P, Fe–P), 2.0 (s, unbound P). ^{11}B NMR (C_6D_6, 128 MHz): δ 60 (v br). ^{29}Si NMR (C_6D_6, 99 MHz): δ 14.4. *Minor species:* δ 12.5. ^{13}C NMR (C_6D_6, 125 MHz): δ 234.4 (t, ^{2}J(C–^{31}P) = 14 Hz, CO), 159.9 (d, J(C–^{31}P) = 27.7 Hz, C^{Ar}), 144.5 (d, J(C–^{31}P) = 9.5 Hz, C^{Ar}), 143.5 (d, J(C–^{31}P) = 16.0 Hz, C^{Ar}), 132.8 (br d, J(C–^{31}P) = 20 Hz, C^{Ar}), 131.3 (s, C^{Ar}), 129.8 (br, C^{Ar}), 127.1 (C^{Ar}), 126.8 (C^{Ar}) 127–124 (v br, C^{Ar}), 30.1 (PCH), 29.9 (PCH), 22 (v br, CCH_3), 21 (v br, CCH_3), 19.3 (CCH_3), 18.5 (CCH_3), 8.0 ($SiCH_2CH_2Si$), −1.3 (br, $SiCH_3$). UV-Vis (DEE, nm {$cm^{-1}M^{-1}$}): 280 {sh}, 400 {sh}, 490 {1300}, 680 (830}. IR (KBr): ν_{CO} = 1856 cm^{-1}. Anal: calcd for $C_{43}H_{70}BFeN_2OP_3Si_2$: C 60.99, H 8.33, N 3.31; found: C 61.06, H 8.29, N 3.35.

(TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 7). *tert*-butyl isocyanide (20 mg, 240 μmol) was added to a dark green solution of **5** (50 g, 61 μmol) in benzene (3 mL), causing a slow color change to inky blue green. After standing for 3 h, lyophilization afforded analytically pure **7** as a black powder (54 mg, 98%). Crystals suitable for XRD were obtained by slow concentration of a tetramethylsilane solution of **7** in a closed vessel containing hexamethyldisiloxane. ^{1}H NMR (C_6D_6, 300 MHz): δ 8.16–8.09 (1H, m, Ar–H), 7.60–6.80 (11H, m, Ar–H), 3.6 (1H, br, PCH), 3.0 (2H, br, PCH), 2.0 (br, 3H, PCH), 1.8–0.8 (12H, v br, $PCCH_3$) 1.62 (6H, dd, ^{3}J(H–P) = 11 Hz, ^{3}J(H–H) = 7 Hz, $PCCH_3$), 1.35 (6H, br dd, ^{3}J(H–P) = 15 Hz, ^{3}J(H–H) = 7 Hz, $PCCH_3$), 1.24 (9H, s, $NC(CH_3)_3$), 1.19–1.07 (12H, m,

$PCCH_3$), 0.56 (4H, s, $SiCH_2CH_2Si$), 0.1 (12H, v br, $SiCH_3$). ^{31}P NMR (C_6D_6, 121 MHz): δ 91.3 (br, Fe–P), 89.4 (br, Fe–P), 0.1 (s, unbound P). ^{11}B NMR (C_6D_6, 128 MHz): δ 50 (v br). ^{29}Si NMR (C_6D_6, 99 MHz): δ 14.5. ^{13}C NMR (C_6D_6, 125 MHz): δ 183.8 (t, $^2J(C–^{31}P)$ = 16 Hz, CN^tBu), 164.3 (d, $J(C–^{31}P)$ = 27.2 Hz, C^{Ar}), 145.3 (d, $J(C–^{31}P)$ = 9.2 Hz, C^{Ar}), 142.3 (d, $J(C–^{31}P)$ = 24.9 Hz, C^{Ar}), 131.2 (C^{Ar}), 126.4 (C^{Ar}), 125.4 (C^{Ar}), 56.3 ($NC(CH_3)_3$), 31.6 (PCH), 30.4 (br PCH), 26–16 (br m, PCH / $PCCH_3$), 8.5 ($SiCH_2CH_2Si$), 0.9 ($SiCH_3$). UV-Vis (DEE, nm {$cm^{-1}M^{-1}$}): 270 {45000}, 400 {sh}, 590 {4000}, 720 {sh}. IR (KBr): ν_{CN} = 1997 cm^{-1}. Anal: calcd for $C_{47}H_{79}BFeN_3P_0Si_2$: C 62.59, H 8.83, N 4.66; found: C 62.36, H 8.60, N 4.25.

(TPBN)FeR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 8). An inky blue green solution of **7** (55 mg, 61 μmol) in benzene (0.5 mL) was stored for 2 weeks at room temperature in the dark, during which time it turned dark brown. The solvent was removed *in vacuo*, and the dark brown residue was washed with small amounts of tetramethylsilane. The remaining beige solid was extracted in pentane (4 mL) to yield a light brown solution that was concentrated by vapor diffusion into hexamethyldisilane. Decantation of the mother liquor and washing with small amounts of cold tetramethylsilane afforded the product as colorless needles suitable for X-ray diffraction (23 mg, 46 %). ^1H NMR (C_6D_6, 400 MHz): δ 163.0, 71.0, 61.0, 36.6, 35.0, 34.5, 30.1, 24.5, 21.9, 11.2, 7.8, 5.5, 4.2, −1.1, −2.0, −4.2, −5.8, −8.0, −12.4, −14.0, −30.2, −36.8, −53.4, −69.4, −75.2, −91.6. ^{31}P NMR (C_6D_6, 121 MHz): δ 56 (br, unbound P). UV-Vis (DEE, nm {$cm^{-1}M^{-1}$}): 275 {19000}, 900 {75}. μ_{eff}(C_6D_6, Evans method, 20 °C): 5.7 μ_B.

Reaction of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (4) with 12-crown-4 (Figure S1). An excess of 12-crown-4 was added to a dark brown solution of **4** in C_6D_6, resulting in the precipitation of dark solids. Hexamethyldisilane was detected in the supernatant by ^1H NMR. Subsequent addition of THF-d_8 caused the solids to dissolve to give a red solution, in which the characteristic ^1H resonances of [(TPB)Fe(N_2)][Na(12-crown-4)$_2$] were observed.

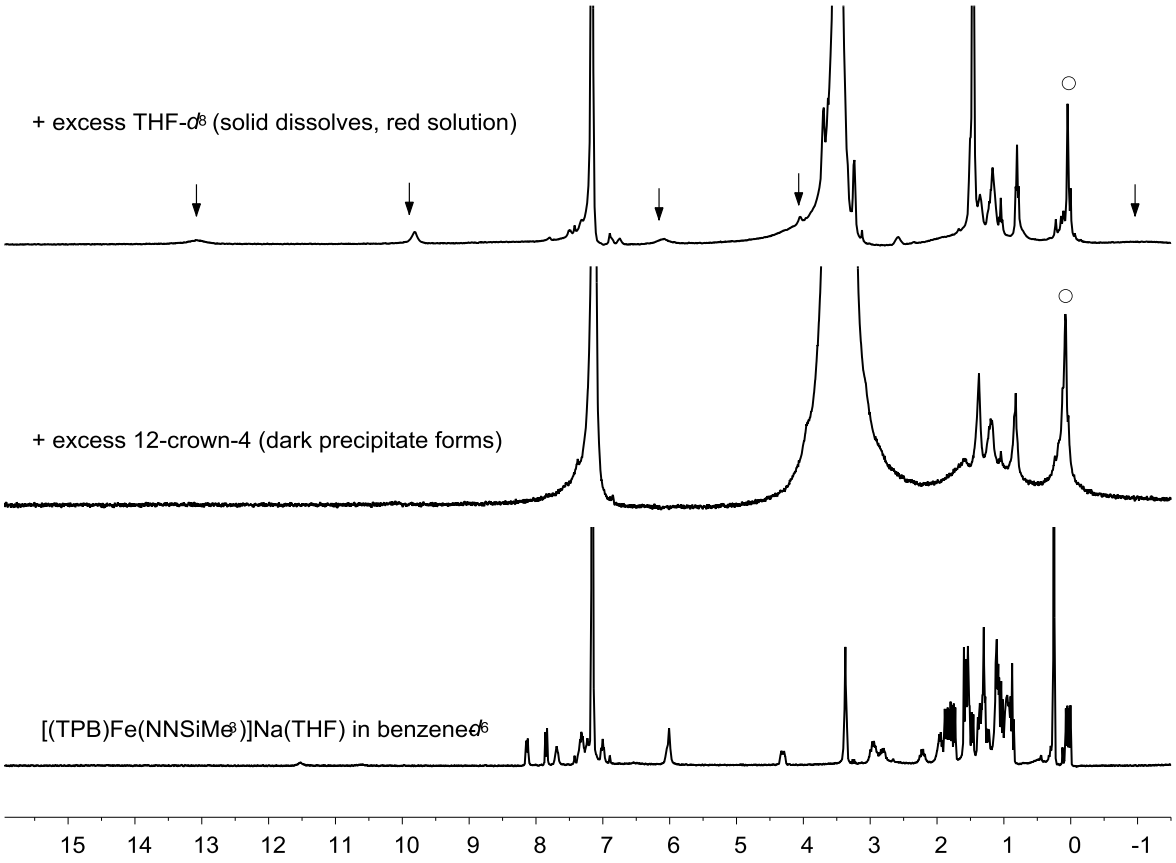

Figure S1. ^{1}H NMR spectra showing the decomposition of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) in the presence of 12-crown-4 in C_6D_6 at room temperature. Arrows mark the characteristic peaks of [(TPB)Fe(N$_2$)]$^{-}$, and ° indicates the characteristic peak of hexamethyldisilane at 0.08 ppm.

NMR Spectra

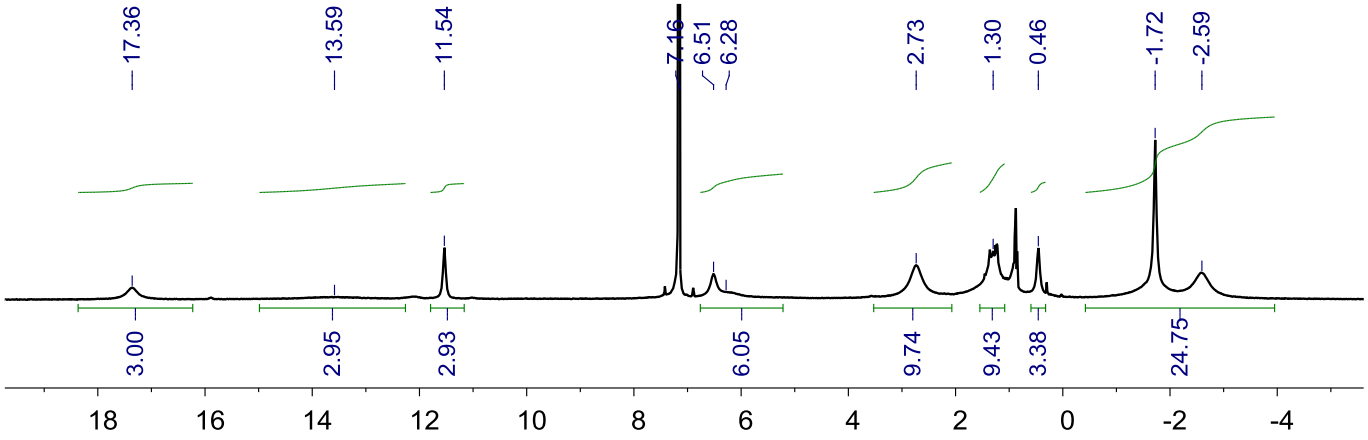

Figure S2. ^{1}H NMR spectrum of (TPB)Fe(NNSiMe$_3$) (**3**) in C_6D_6 at room temperature.

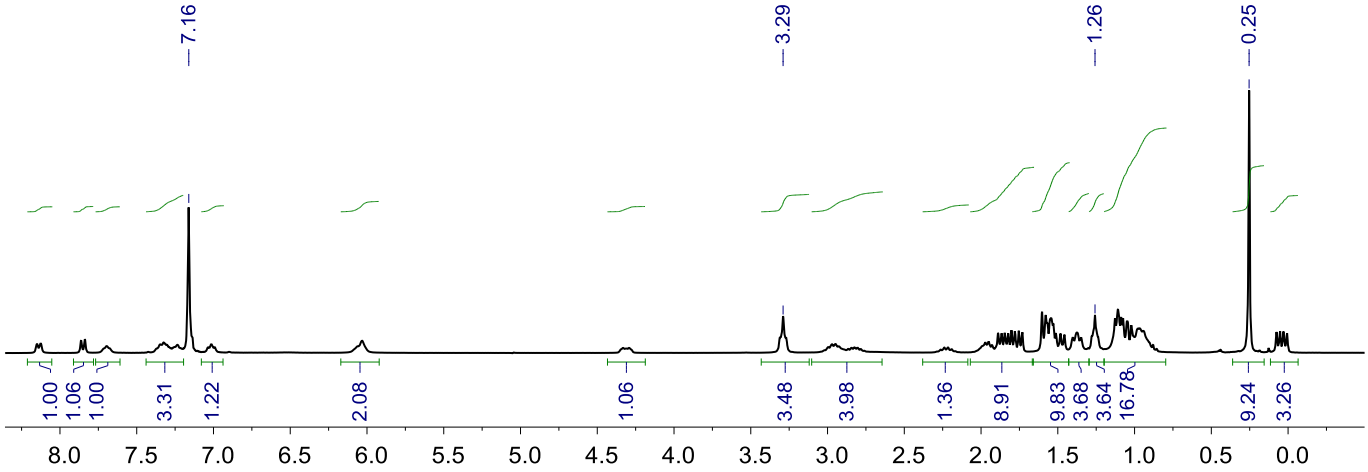

Figure S3. ^{1}H NMR spectrum of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) in C_6D_6 at room temperature.

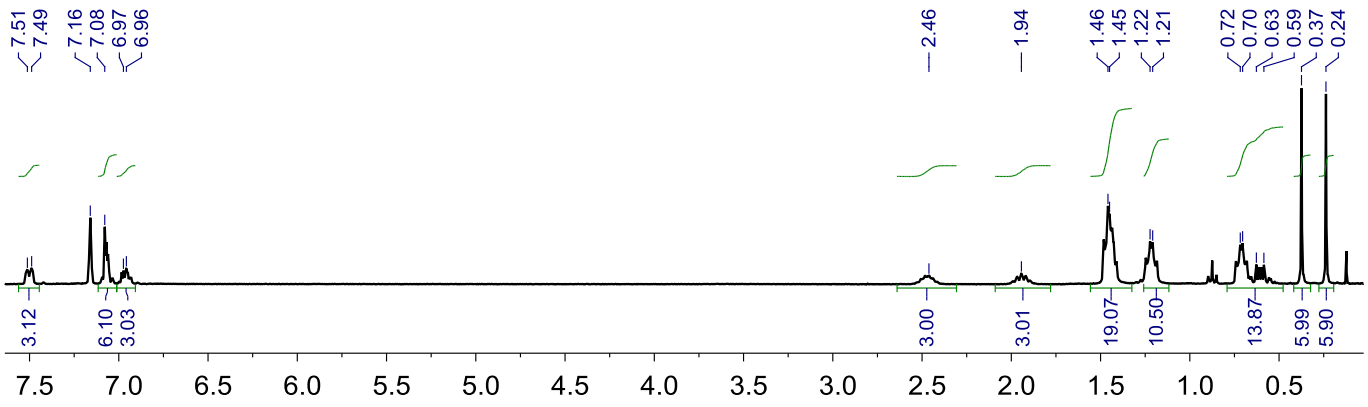

Figure S4. ^{1}H NMR spectrum of (TPB)FeNR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **5**) in C_6D_6 at room temperature.

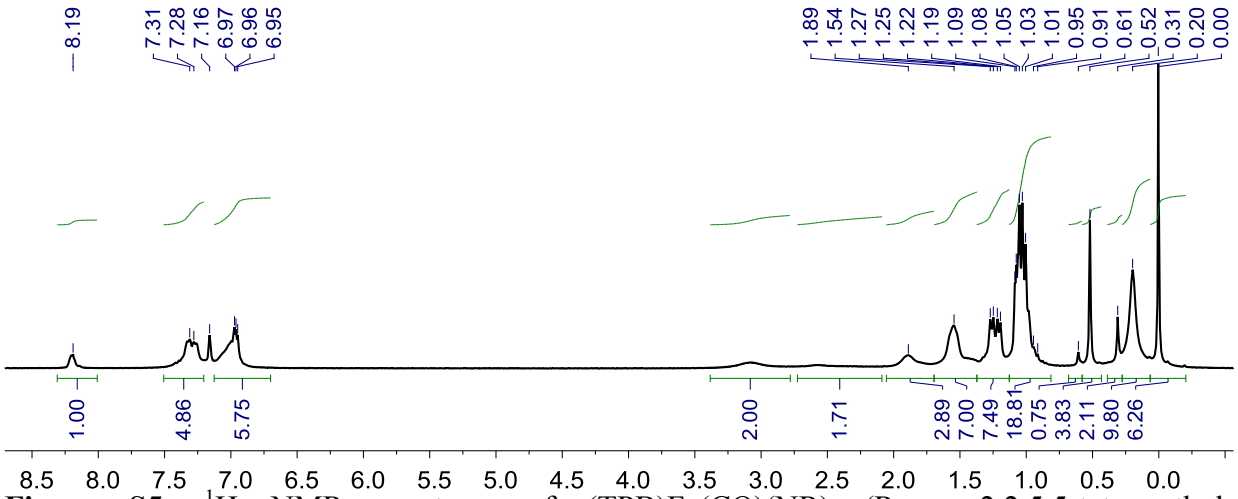

Figure S5. ^{1}H NMR spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**). in C_6D_6 at room temperature.

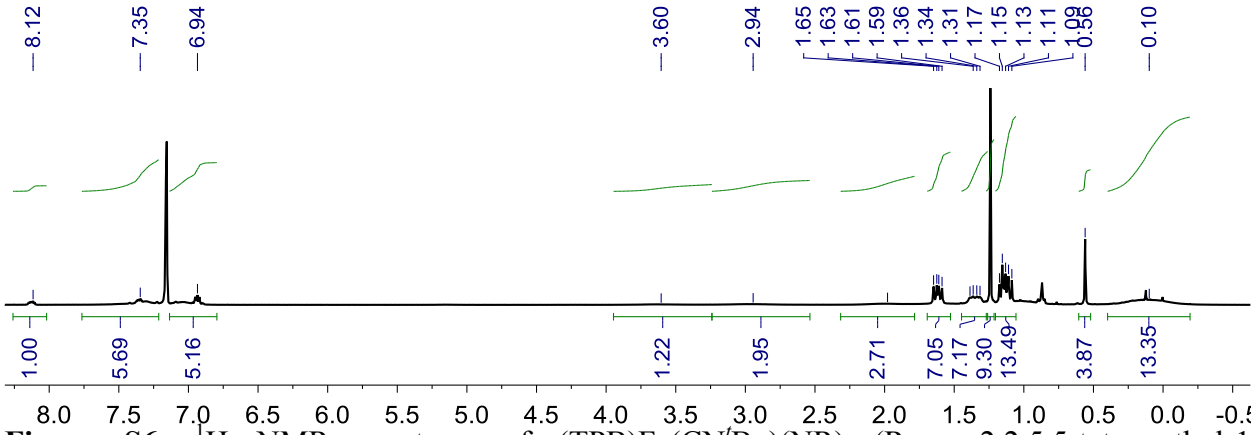

Figure S6. ^{1}H NMR spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**). in C_6D_6 at room temperature.

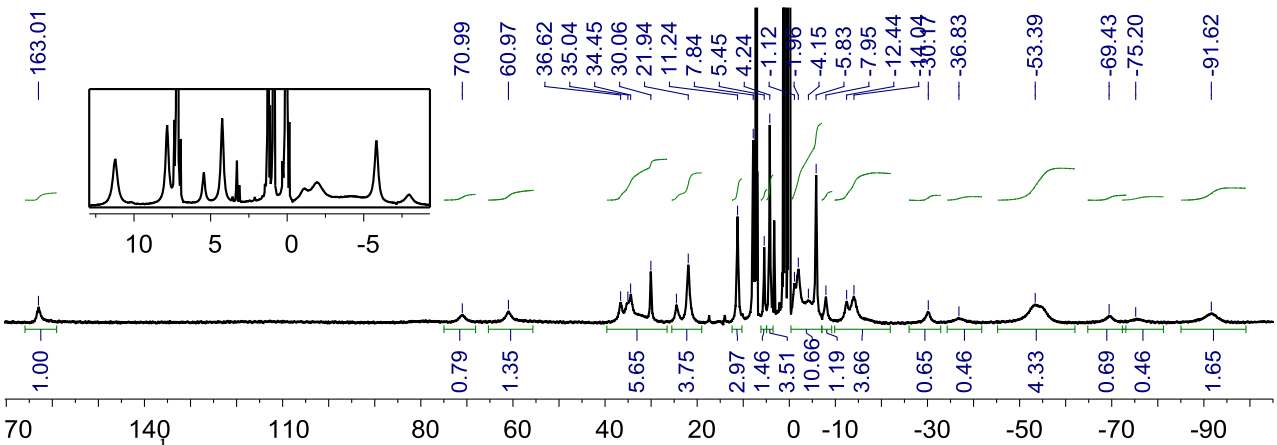

Figure S7. ^{1}H NMR spectrum of (TPBN)FeR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **8**) in C_6D_6 at room temperature.

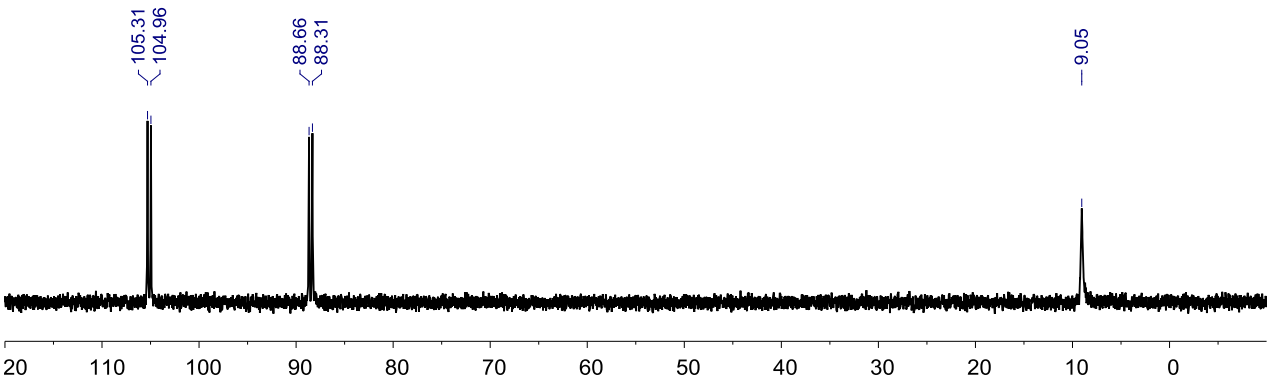

Figure S8. ^{31}P NMR spectrum of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) in C_6D_6 at room temperature.

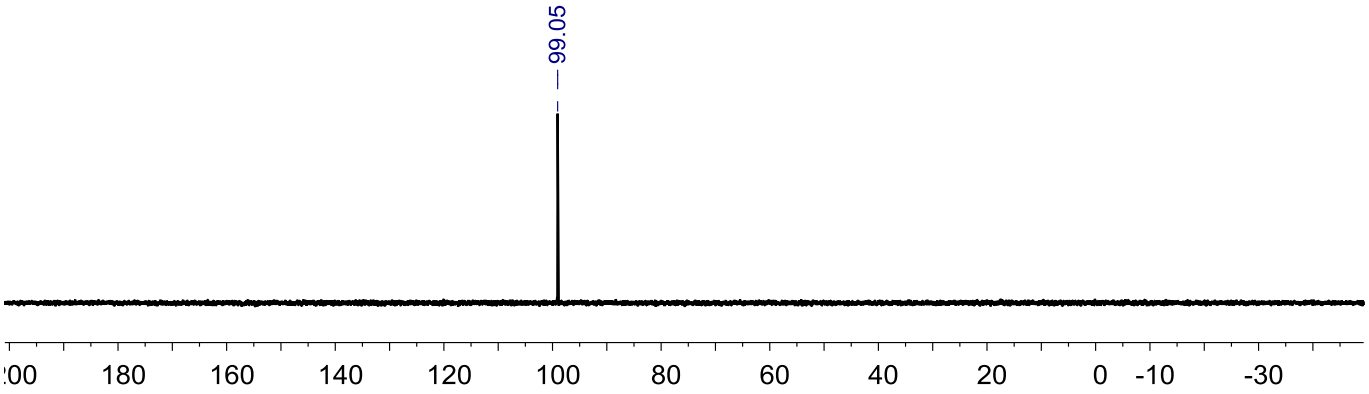

Figure S9. ^{31}P NMR spectrum of (TPB)FeNR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **5**). in C_6D_6 at room temperature.

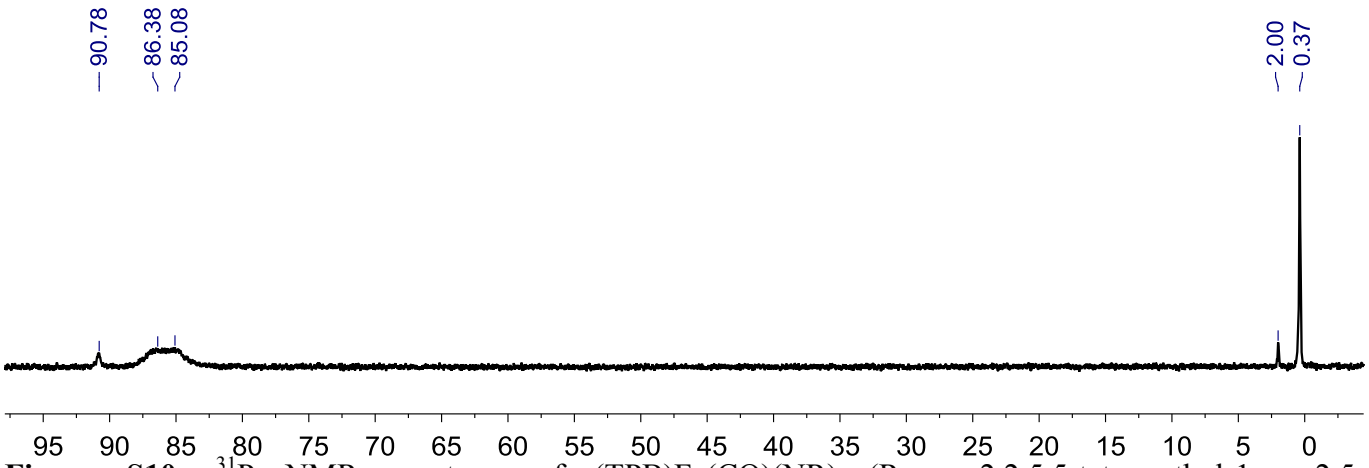

Figure S10. ^{31}P NMR spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**) in C_6D_6 at room temperature.

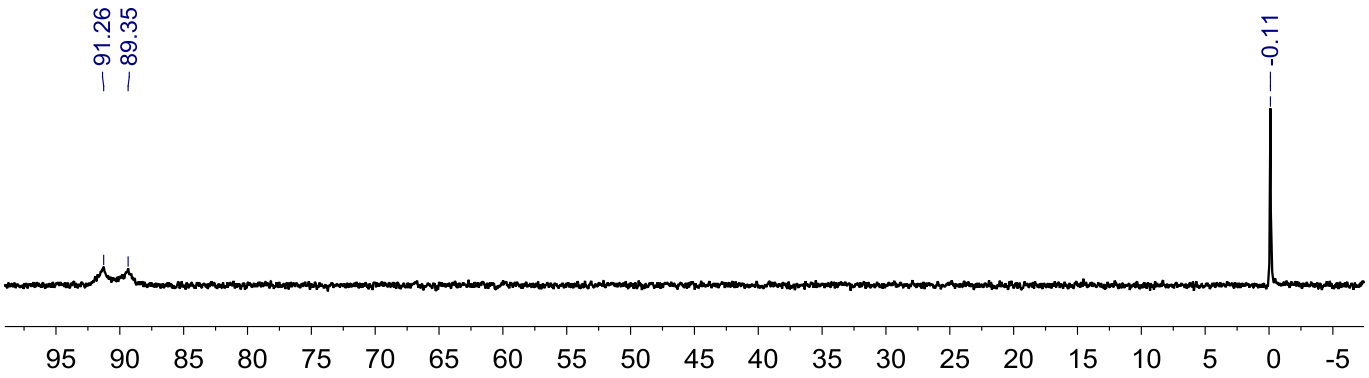

Figure S11. ^{31}P NMR spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**) in C_6D_6 at room temperature.

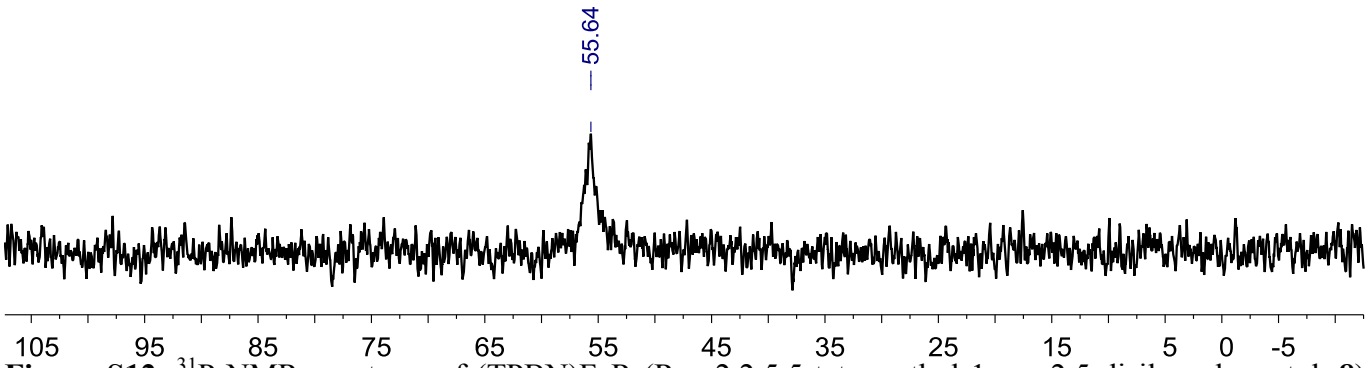

Figure S12. ^{31}P NMR spectrum of (TPBN)FeR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **8**) in C_6D_6 at room temperature.

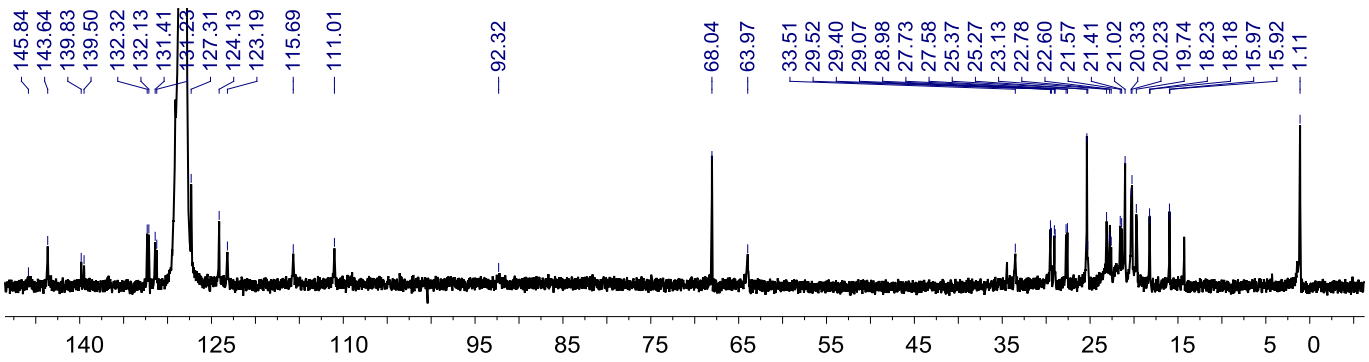

Figure S13. ^{13}C NMR spectrum of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) in C_6D_6 at room temperature.

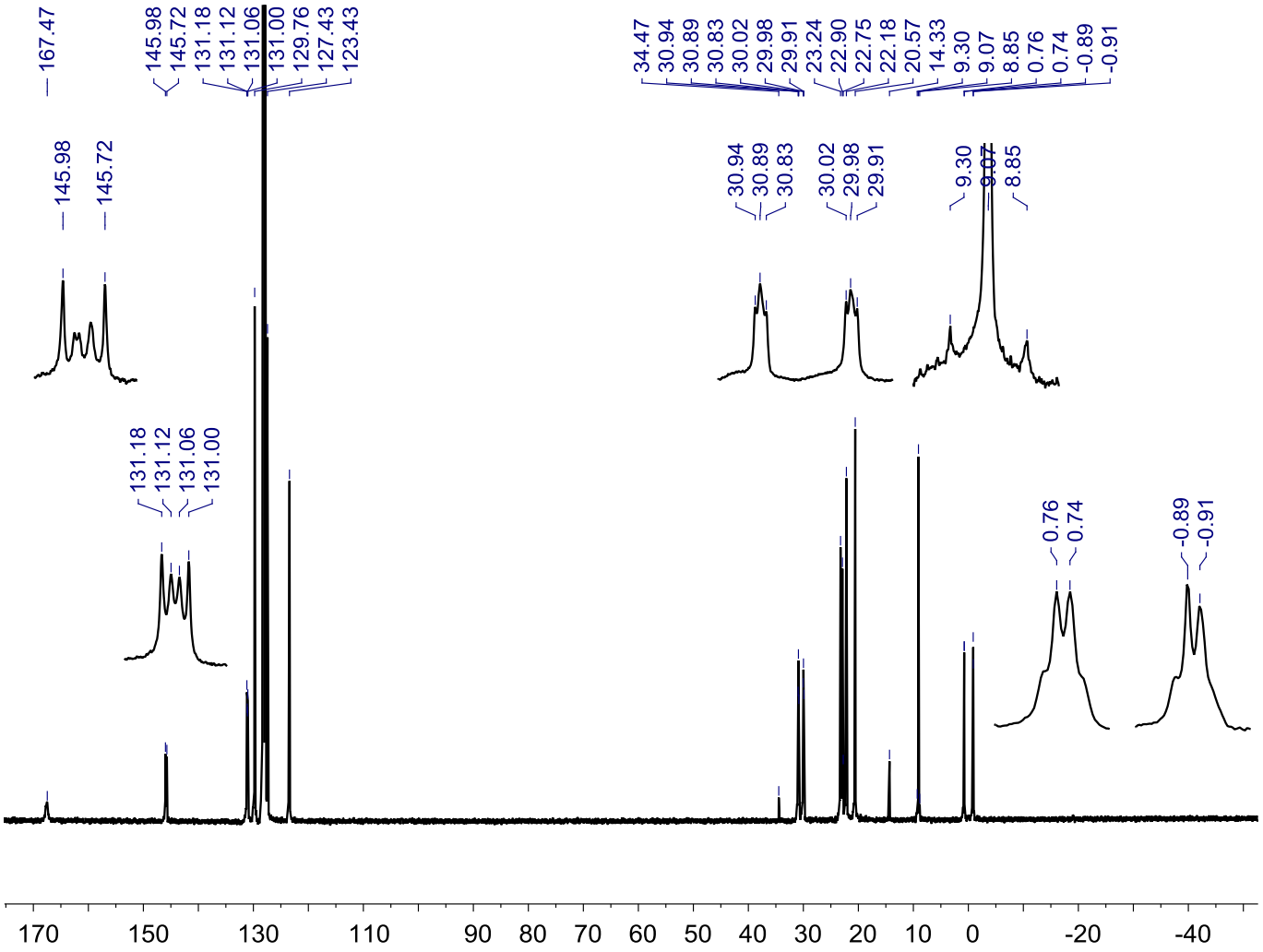

Figure S14. ^{13}C NMR spectrum of (TPB)FeNR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **5**). in C_6D_6 at room temperature.

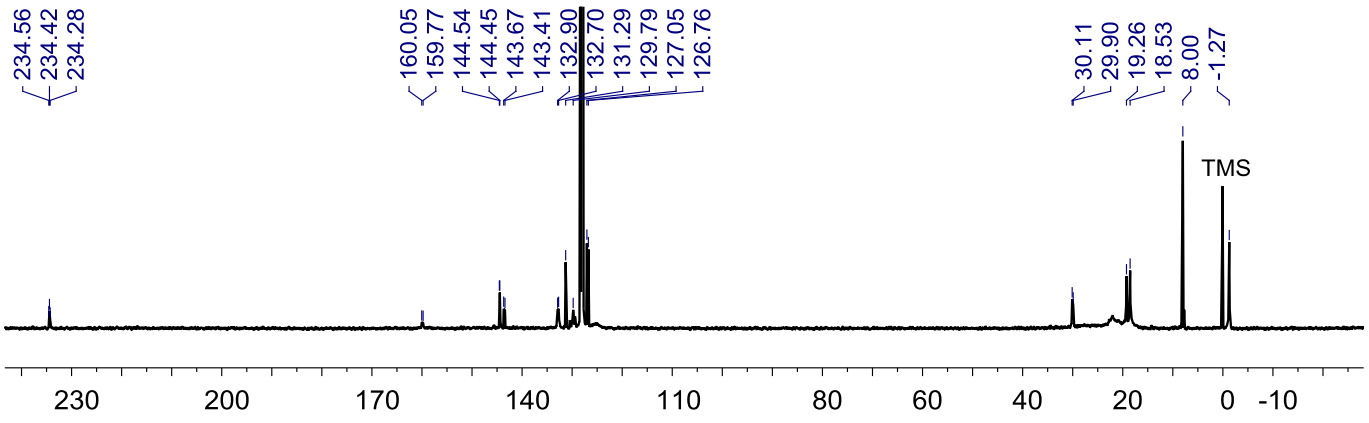

Figure S15. ^{13}C NMR spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**) in C_6D_6 at room temperature.

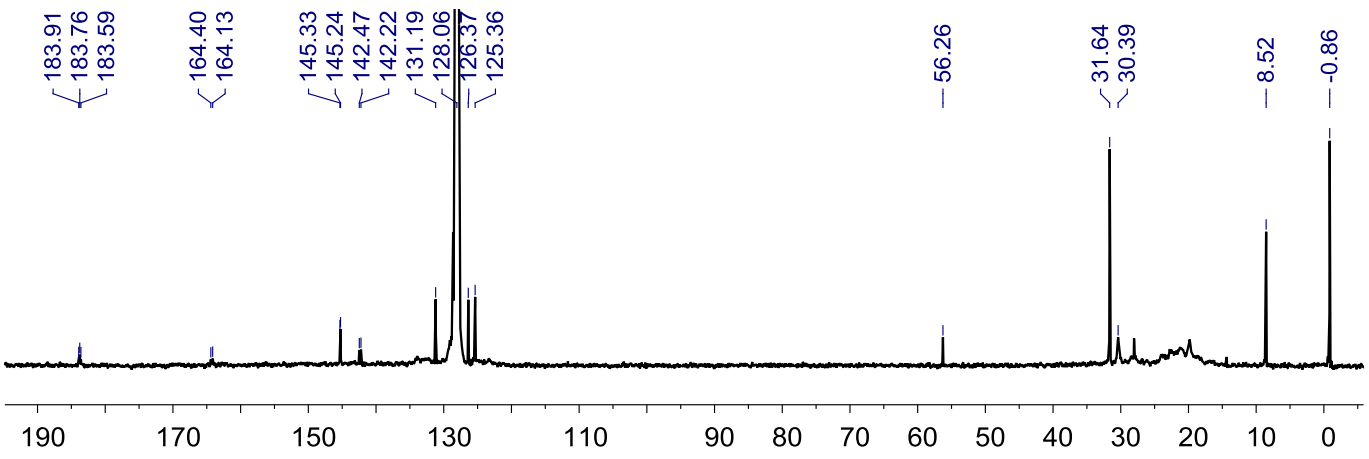

Figure S16. ^{13}C NMR spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**) in C_6D_6 at room temperature.

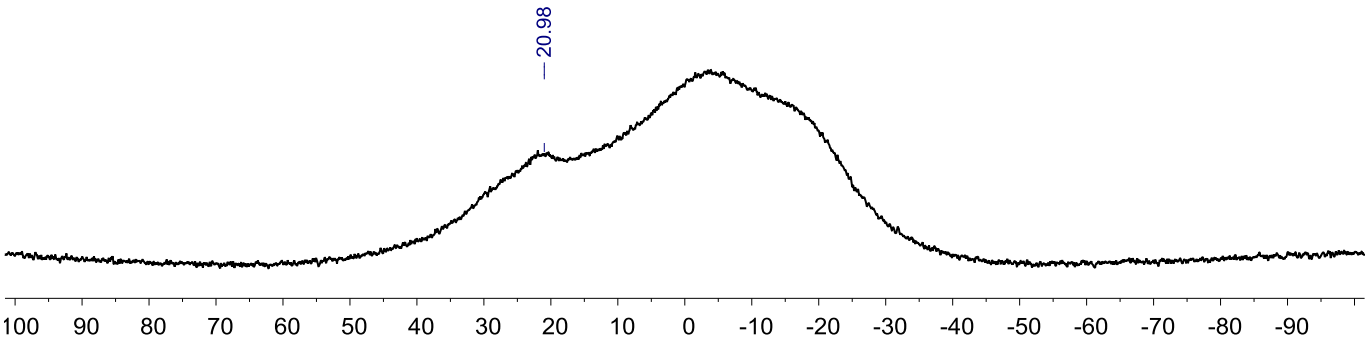

Figure S17. ^{11}B NMR spectrum of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) in C_6D_6 at room temperature.

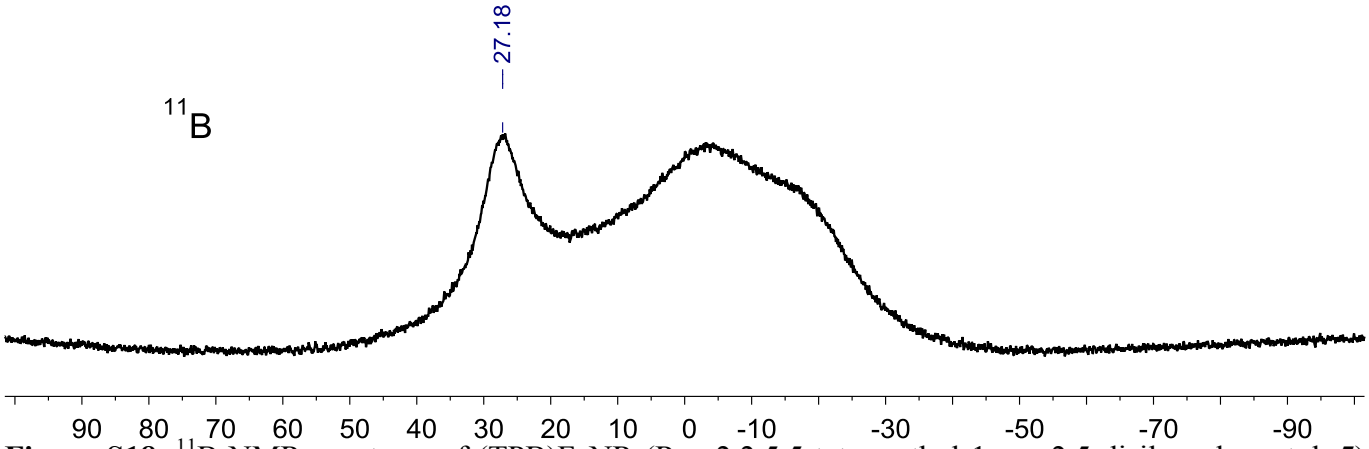

Figure S18. ^{11}B NMR spectrum of (TPB)FeNR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **5**) in C_6D_6 at room temperature.

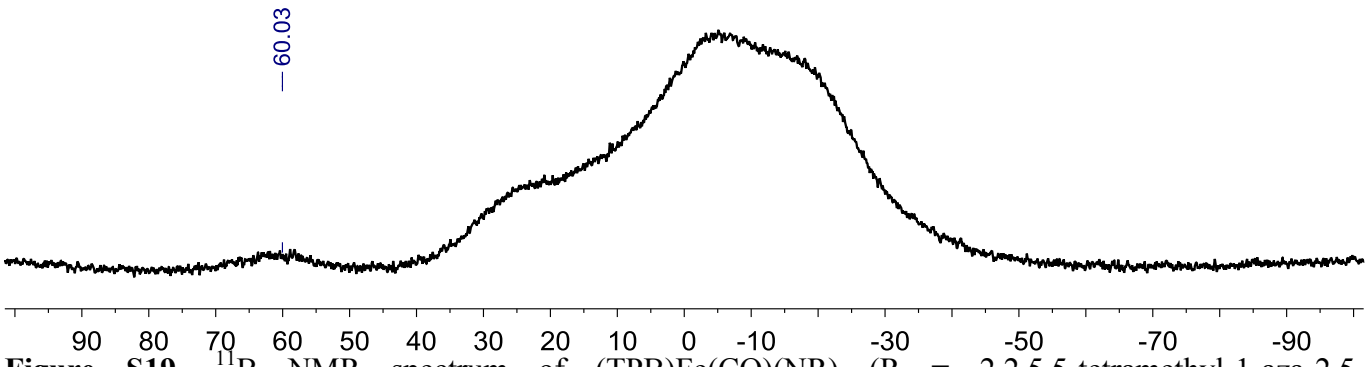

Figure S19. ^{11}B NMR spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**) in C_6D_6 at room temperature.

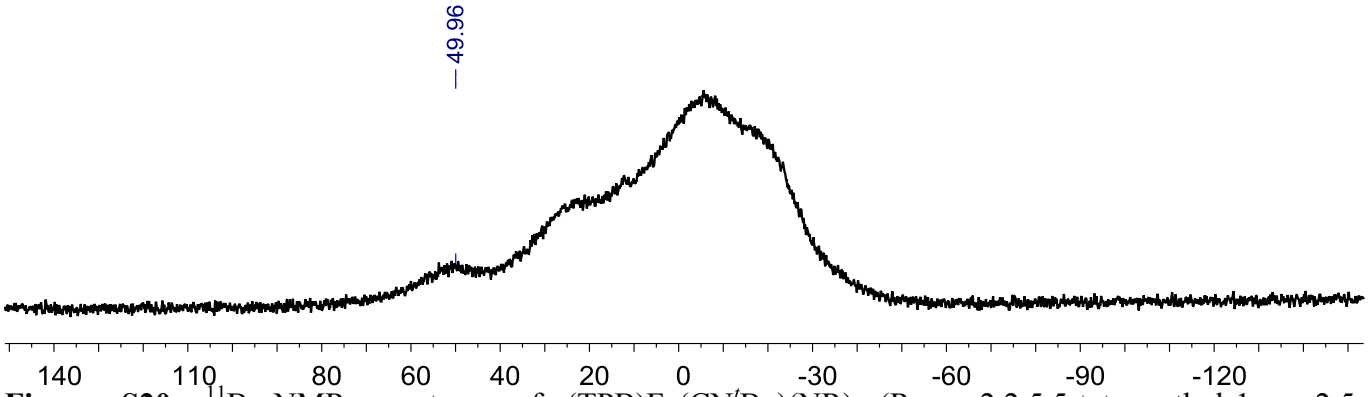

Figure S20. ^{11}B NMR spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**) in C_6D_6 at room temperature.

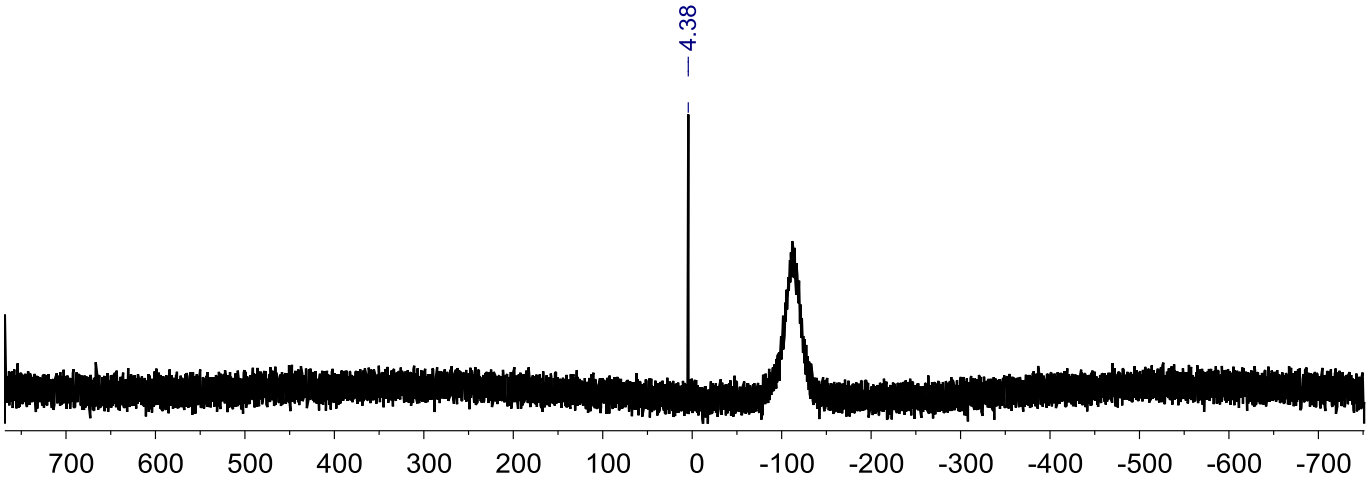

Figure S21. ^{29}Si NMR spectrum of (TPB)FeNR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **5**) in C_6D_6 at room temperature.

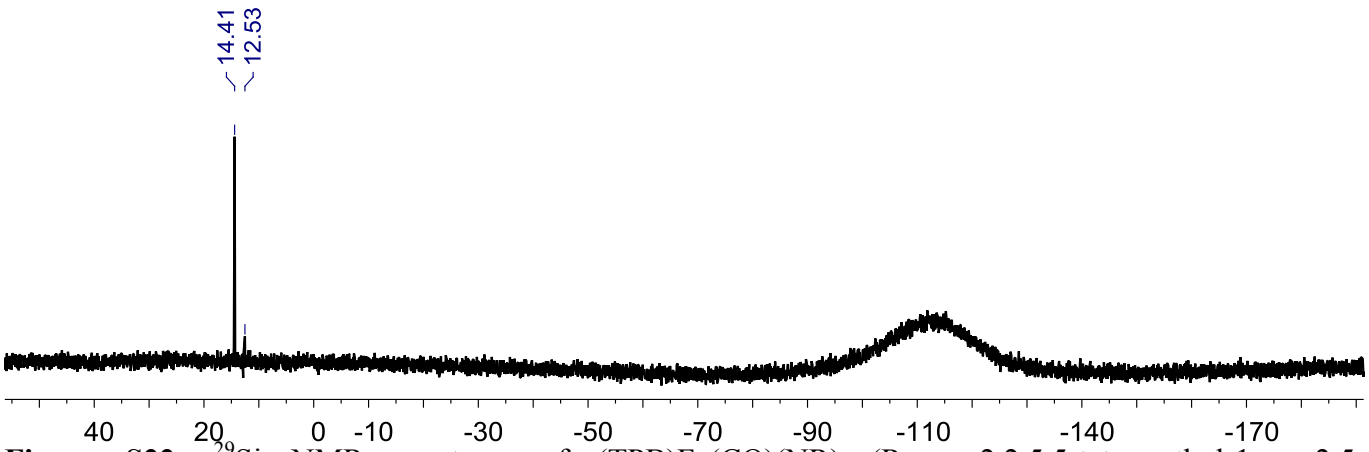

Figure S22. ^{29}Si NMR spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**) in C_6D_6 at room temperature.

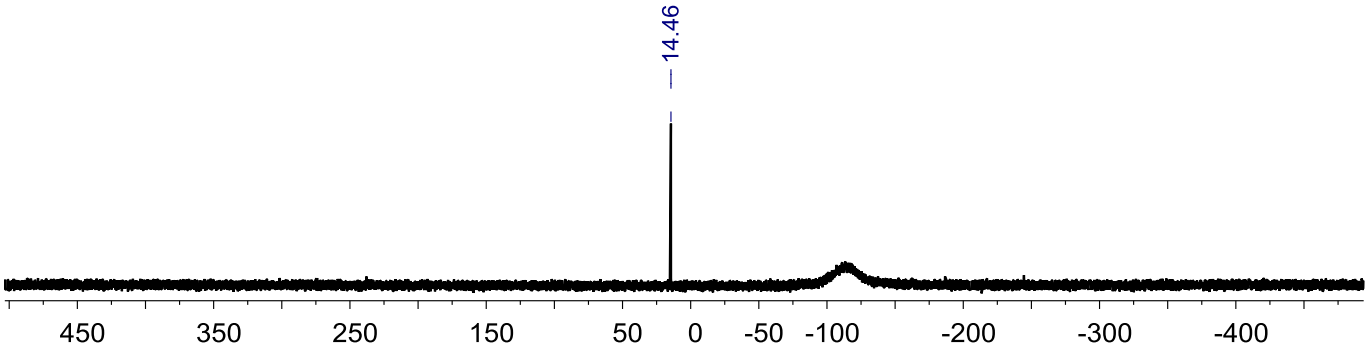

Figure S23. ^{29}Si NMR spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**) in C_6D_6 at room temperature

EPR Spectra

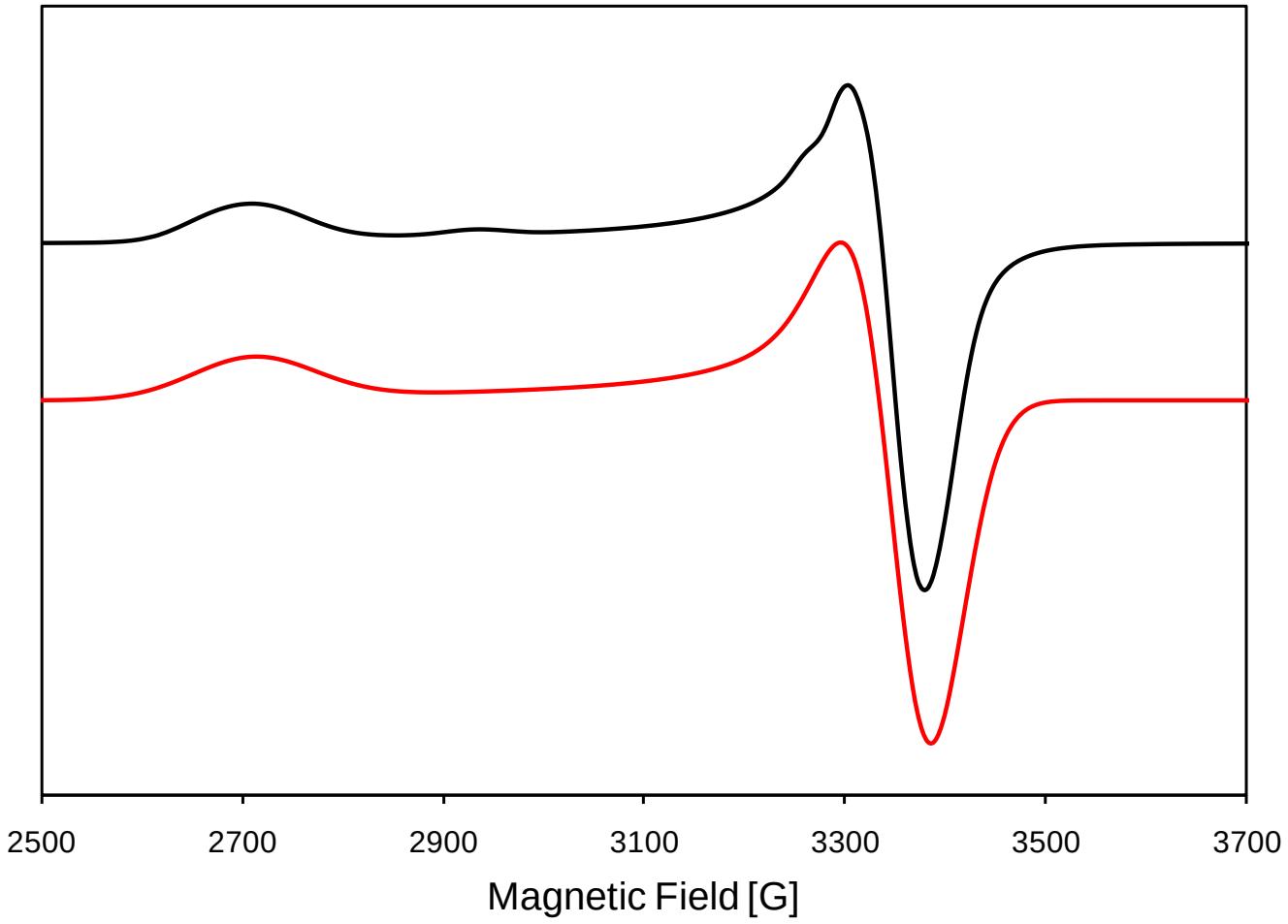

Figure S24. X-band EPR spectrum of (TPB)Fe(NNSiMe$_3$) (**3**) in Toluene at 20 K (black) ant simulated spectrum (red). Simulation parameters: g_x = 1.990, g_y = 2.005, g_z = 2.480, HStrain$_x$ = 250, HStrain$_y$ = 250, Hstrain$_z$ = 500.

IR Spectra

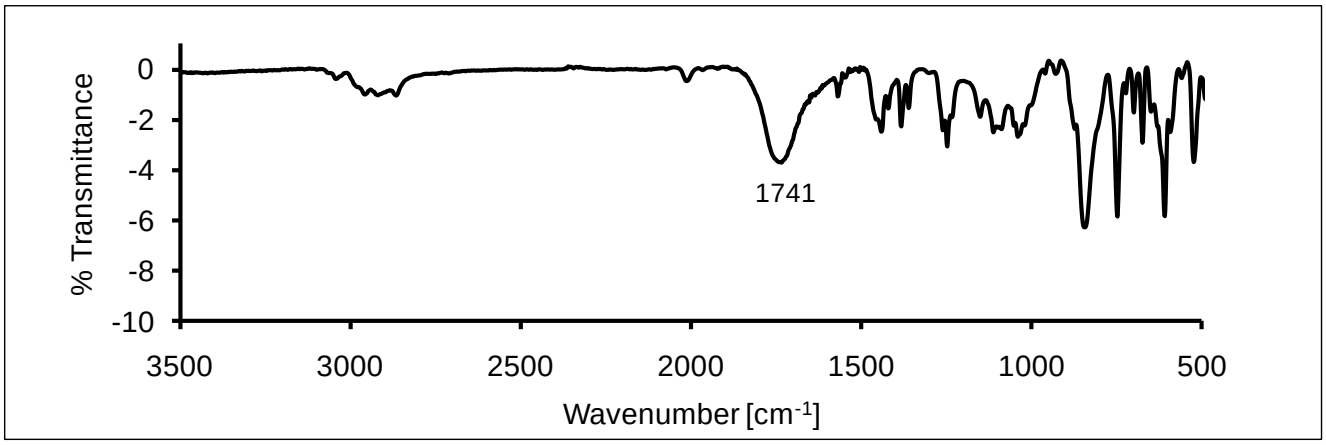

Figure S25. IR spectrum of (TPB)Fe(NNSiMe$_3$) **(3)** in a KBr pellet.

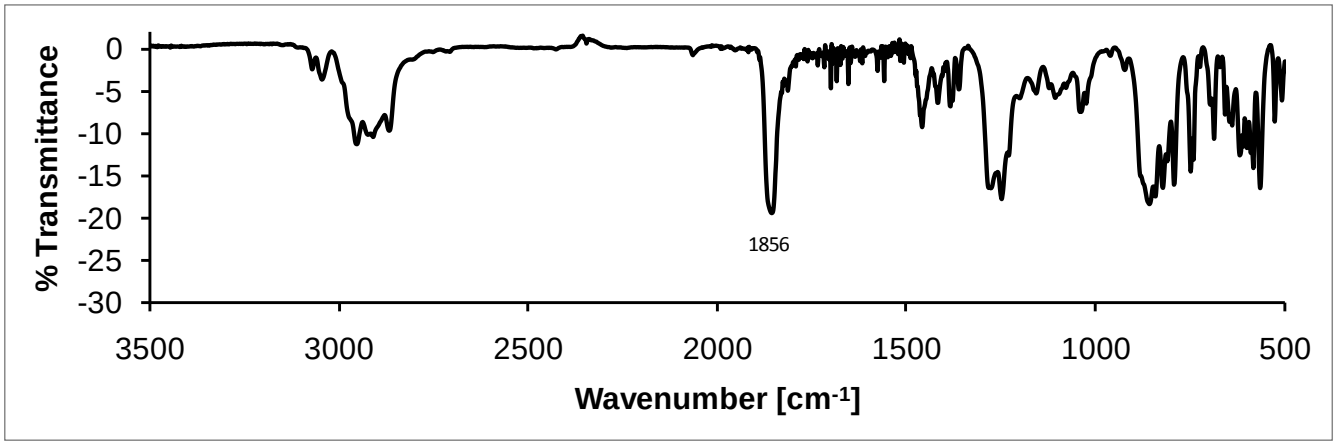

Figure S26. IR spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**) in a KBr pellet.

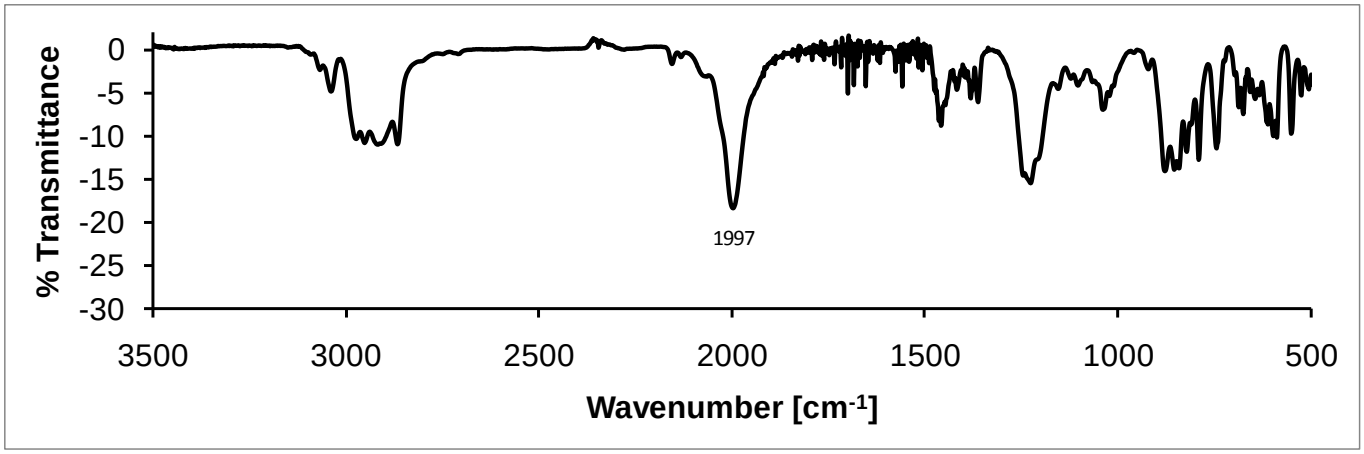

Figure S27. IR spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**) in a KBr pellet.

UV-Vis Spectra

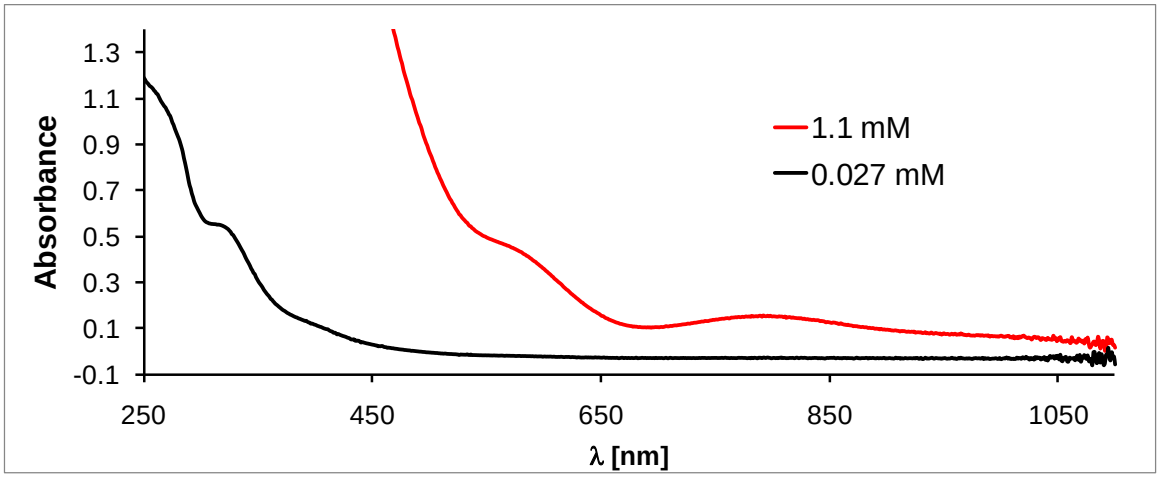

Figure S28. UV-Vis spectrum of (TPB)Fe(NNSiMe$_3$) (**3**) in diethylether

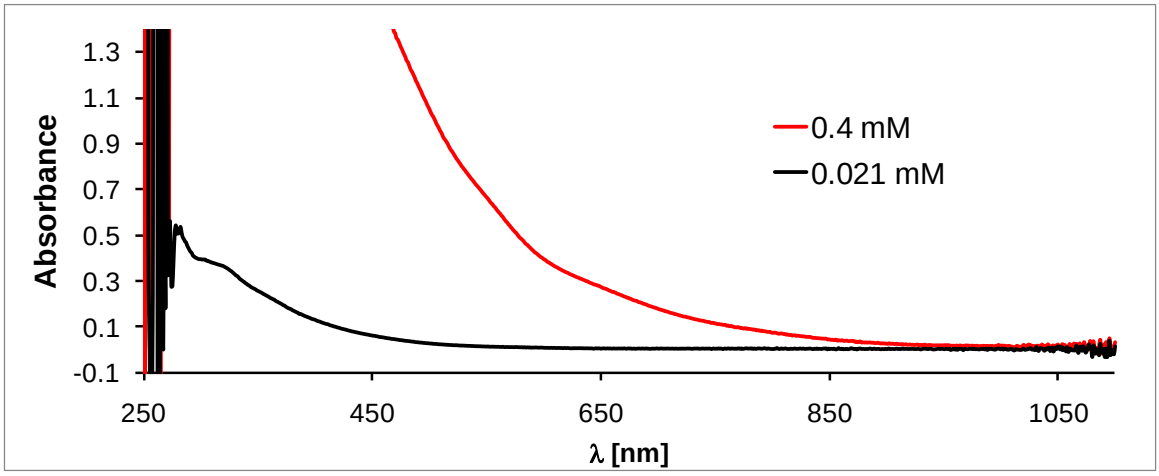

Figure S29. UV-Vis spectrum of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**) in benzene

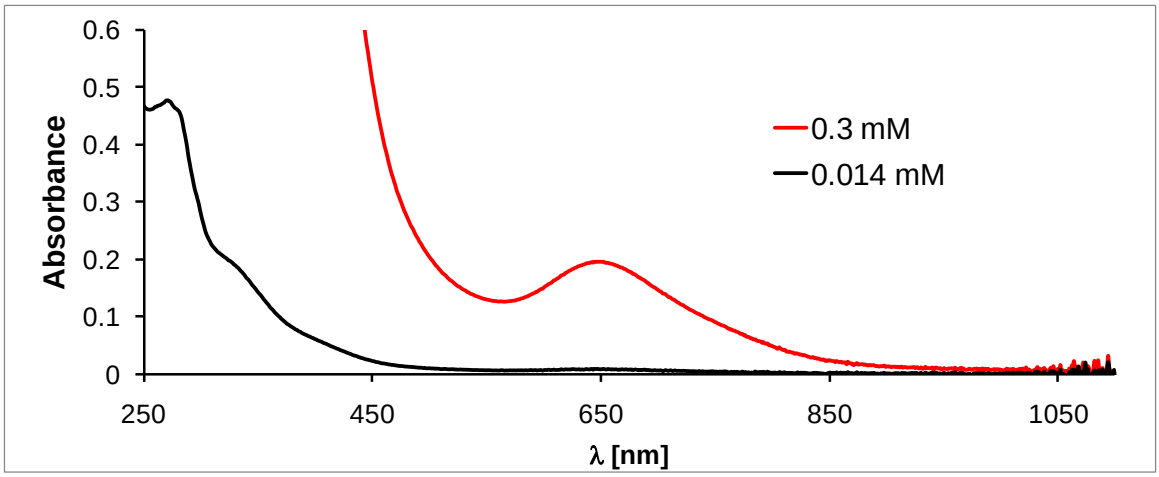

Figure S30. UV-Vis spectrum of (TPB)FeNR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **5**) in diethyl ether.

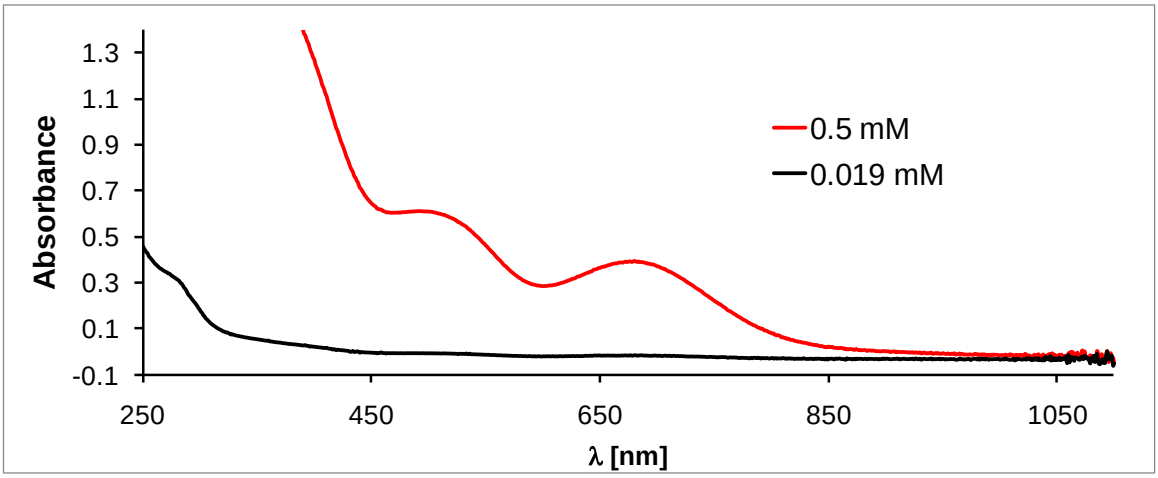

Figure S31. UV-Vis spectrum of (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **6**) in diethyl ether.

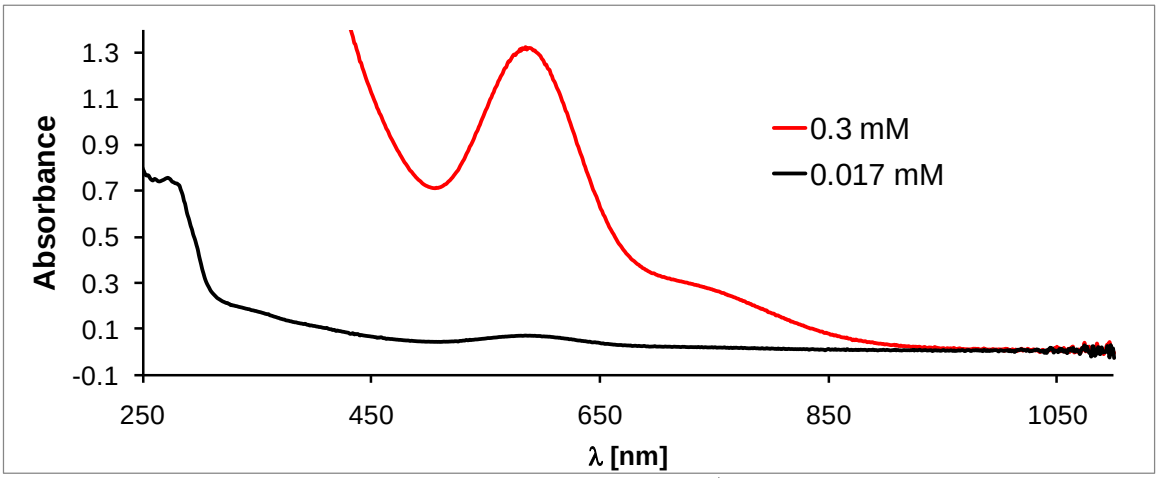

Figure S32. UV-Vis spectrum of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**) in diethyl ether.

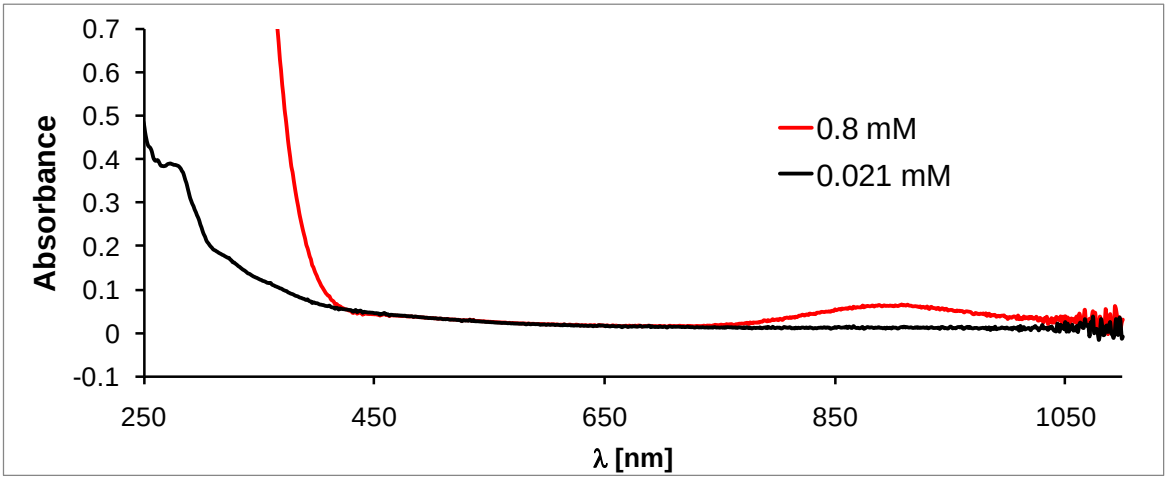

Figure S33. UV-Vis spectrum of (TPBN)FeR (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **8**) in diethyl ether.

X-Ray Diffraction Data

Table 1: Crystallographic Data for Compounds **3, 4, 6, 7, 8**

	3	**4**	**6**	**7**	**8**
chem formula	$C_{39}H_{62}BFeN_2P_3Si \cdot 1/2\ C_5H_{12}$	$C_{43}H_{71}BFeN_2NaOP_3Si$	$C_{47}H_{82}BFeN_2OP_3Si_3$	$C_{47}H_{79}BFeN_3P_3Si_2$	$C_{42}H_{70}BFeN_2P_3Si_2$
fw	782.64	842.67	934.99	901.88	818.8
cryst syst	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
space group	P -1	P $2_1/c$	P -1	Pbca	P $2_1/c$
a [Å]	10.7723(5)	20.6183(11)	12.0358(4)	11.2149(5)	23.4418(10)
b [Å]	11.3518(5)	11.3406(6)	12.2087(5)	24.117(1)	9.6272(4)
c [Å]	20.4380(9)	19.2147(10)	19.5934(7)	37.5403(13)	22.5854(9)
α [°]	78.098(2)	90	107.196(2)	90	90
β [°]	78.462(2)	90.439(3)	91.580(2)	90	116.834(2)
γ [°]	62.107(2)	90	101.338(2)	90	90
V [$Å^3$]	2145.87(17)	4492.7(4)	2685.40(18)	10153.5(7)	4548.2(3)
Z	2	4	2	8	4
D_{calcd} [g cm^{-3}]	1.211	1.246	1.156	1.180	1.196
F(000)	842.0	1808.8	1008.0	3888.0	1760.0
μ [mm^{-1}]	0.522	0.513	0.471	0.472	0.520
temp. [K]	100	100	100	100	100
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
measd rflns	164557	109388	328888	121411	169811
unique rflns	20777	9182	45761	8661	22030
data/restraints/param	20777/561/134	9182/4/505	45761/108/645	8661/0/533	22030/0/476
R(F) ($I>2\sigma(I)$)	0.0350	0.0510	0.0374	0.0504	0.0392
wR(F^2) (all)	0.1065	0.1071	0.1012	0.1025	0.0963
GOF	1.035	0.997	1.010	1.144	1.097

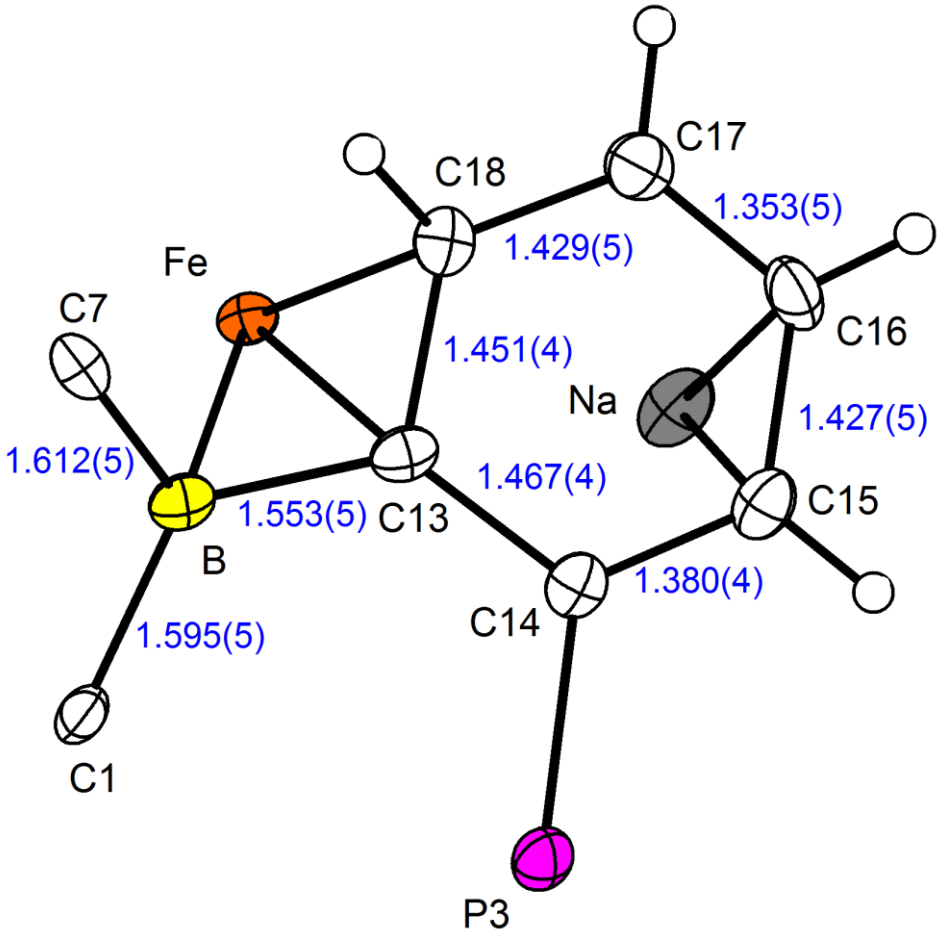

Figure S34. Experimental bond lengths supporting a partial dearomatization of the bound phenylene in of [(TPB)Fe(NNSiMe$_3$)]Na(THF) (**4**).

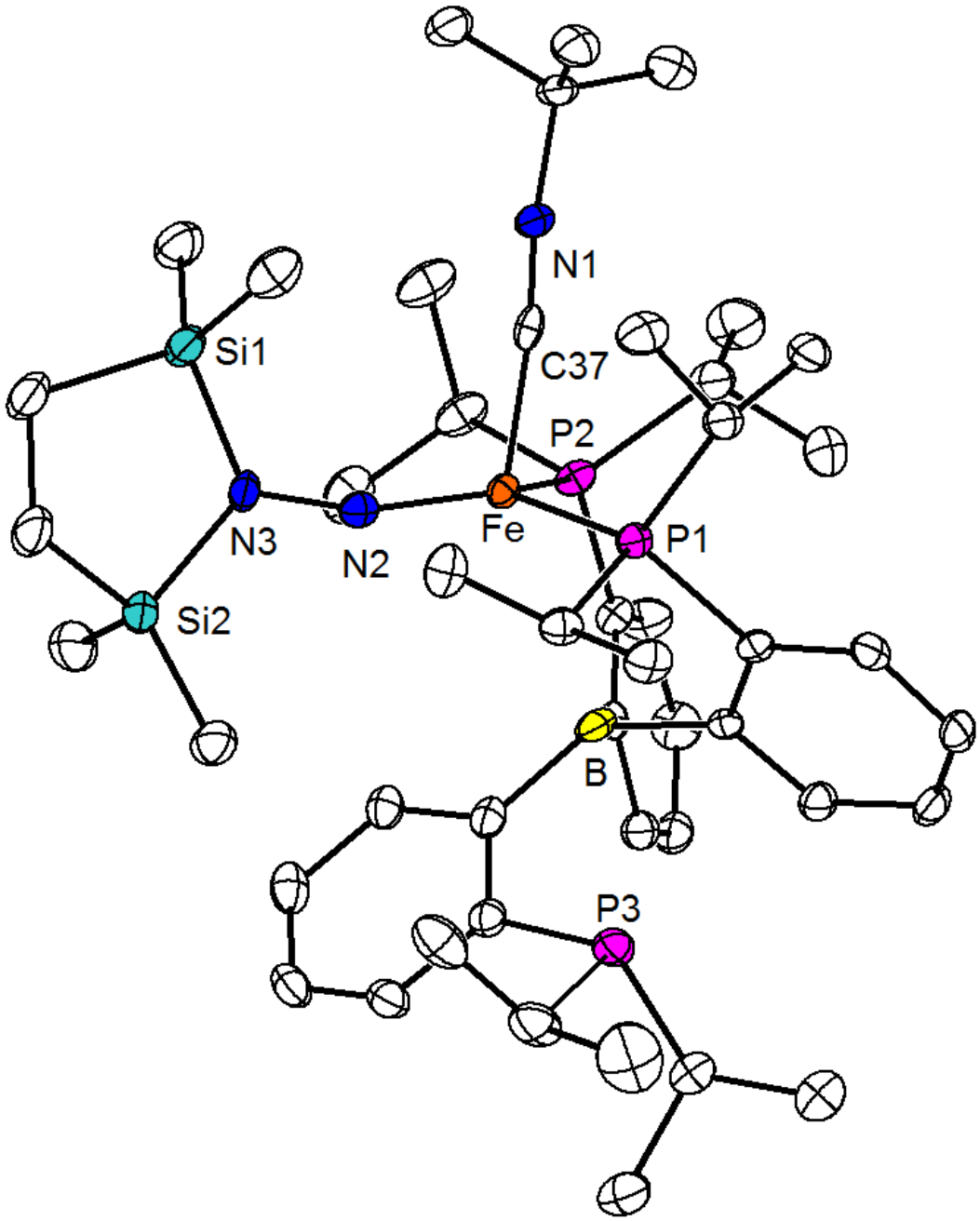

Figure S35. Solid state structure of (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, **7**). Thermal ellipsoids set at 50%.

DFT Calculations

Optimized Coordinates [Å] for (TPB)Fe(N_2)

Atom	X	Y	Z
Fe	-0.011033	-0.050846	-0.895149
P	-0.406562	2.345098	-0.669919
P	-2.054592	-1.370349	-0.524911
P	2.327131	-0.830895	-0.636356
N	-0.002750	-0.170196	-2.771960
N	0.022527	-0.277352	-3.897433
C	0.385204	2.640981	0.959893
C	1.050873	-1.214245	1.779803
C	-1.448441	-0.283806	1.935905
C	2.151047	-1.649324	0.993588
C	-2.409294	-1.066534	1.252683
C	0.582223	1.484862	1.759994
B	0.040460	0.004612	1.325699
C	-3.586167	-1.500294	1.888535
H	-4.285461	-2.149836	1.370960
C	-3.874994	-1.109791	3.193304
H	-4.789278	-1.445632	3.676062
C	-2.982863	-0.267759	3.861349
H	-3.205081	0.068726	4.871938
C	-1.798907	0.127205	3.241034
H	-1.113107	0.767898	3.789760
C	0.883763	-1.883924	3.012955
H	0.045473	-1.611237	3.647723
C	1.744495	-2.889157	3.452910
H	1.568551	-3.368972	4.413516
C	2.822752	-3.287216	2.661237
H	3.492728	-4.077747	2.989885
C	3.019491	-2.663939	1.431522
H	3.843706	-2.989515	0.802276
C	1.237112	1.691607	2.993284
H	1.436349	0.831268	3.628418
C	1.656956	2.950671	3.420999
H	2.158718	3.058678	4.380392
C	1.446360	4.071759	2.614618
H	1.781125	5.055323	2.934442
C	0.812140	3.911185	1.384472
H	0.671494	4.779773	0.745831
C	-3.606004	-0.685158	-1.414623
H	-3.835474	0.210856	-0.825355
C	-4.857738	-1.579387	-1.401427
H	-5.693004	-1.034826	-1.860090
H	-4.714951	-2.496363	-1.982793
H	-5.171697	-1.859210	-0.393664
C	-3.304229	-0.228778	-2.852290
H	-2.540074	0.550720	-2.883608
H	-2.958836	-1.052610	-3.485738
H	-4.216737	0.176576	-3.308356
C	-2.199356	-3.241402	-0.710596
H	-3.220239	-3.495946	-0.396699
C	-2.015623	-3.702577	-2.164381
H	-1.032407	-3.423570	-2.554558
H	-2.096942	-4.795407	-2.222151
H	-2.769424	-3.280567	-2.836052
C	-1.225407	-3.951035	0.241296
H	-0.187188	-3.675933	0.036577
H	-1.429332	-3.702671	1.286219
H	-1.316838	-5.038354	0.123681
C	2.952509	-2.164874	-1.823602
H	3.862131	-2.583982	-1.377467
C	1.950616	-3.310979	-1.990416
H	1.720863	-3.792045	-1.035784
H	1.015216	-2.955683	-2.432573
H	2.364999	-4.074864	-2.660796
C	3.319465	-1.561521	-3.191080
H	3.711590	-2.348081	-3.848240
H	2.445002	-1.127299	-3.683802
H	4.086618	-0.784424	-3.118821
C	3.880897	0.271746	-0.514876
H	3.875403	0.838888	-1.454784
C	5.212151	-0.493924	-0.415729
H	6.034462	0.229106	-0.342386
H	5.245674	-1.113712	0.486817
H	5.418439	-1.130373	-1.280008
C	3.794663	1.266840	0.647827
H	2.899954	1.886019	0.607974
H	3.791334	0.746459	1.610692
H	4.670467	1.927981	0.627154
C	-2.141834	3.121776	-0.553034
H	-2.653338	2.766148	-1.457859
C	-2.907294	2.602488	0.671360
H	-2.945627	1.514296	0.718565
H	-2.442229	2.948755	1.600057
H	-3.936718	2.982153	0.649156
C	-2.170897	4.659674	-0.548566
H	-3.212133	4.999878	-0.480735
H	-1.642277	5.061895	0.322561
H	-1.741646	5.106897	-1.449045
C	0.444087	3.498026	-1.901508
H	0.359921	4.518746	-1.508551
C	-0.261786	3.438845	-3.267707
H	0.222012	4.133267	-3.966111
H	-0.199110	2.436611	-3.702579
H	-1.319389	3.715247	-3.211438
C	1.935940	3.176333	-2.055846
H	2.474225	3.272533	-1.109337
H	2.084533	2.159253	-2.435010
H	2.392559	3.868651	-2.774671

Total Energy [a.u.]: -3826.4495232

Optimized Coordinates [Å] for (TPB)Fe(N_2)]$^-$

Atom	X	Y	Z
Fe	-0.049071	-0.072109	-0.927668

P	-0.418802	2.149328	-0.556357
P	-1.997882	-1.176904	-0.559802
P	2.250533	-0.644067	-0.674142
N	-0.065469	-0.164944	-2.703923
N	-0.065228	-0.274229	-3.844780
C	0.359377	2.496802	1.083238
C	1.107185	-1.331267	1.718515
C	-1.400179	-0.485029	2.003225
C	2.207205	-1.639723	0.874026
C	-2.392724	-1.146433	1.244683
C	0.564450	1.329365	1.863235
B	0.050581	-0.129312	1.318754
C	-3.558048	-1.650919	1.845822
H	-4.277734	-2.221155	1.265261
C	-3.810570	-1.435248	3.200330
H	-4.721578	-1.818174	3.656888
C	-2.888088	-0.704557	3.953224
H	-3.082993	-0.502230	5.006007
C	-1.709006	-0.250762	3.361375
H	-0.999153	0.302598	3.972738
C	1.000424	-2.121197	2.886780
H	0.165318	-1.948186	3.560731
C	1.913042	-3.125856	3.210339
H	1.779164	-3.706056	4.122940
C	2.991271	-3.395339	2.365401
H	3.701149	-4.185971	2.601445
C	3.132528	-2.645205	1.198080
H	3.954587	-2.873198	0.523610
C	1.196685	1.518161	3.110494
H	1.405010	0.645932	3.728474
C	1.596206	2.775012	3.569554
H	2.089335	2.871097	4.536462
C	1.377636	3.908424	2.783442
H	1.697898	4.890959	3.125755
C	0.756085	3.762991	1.541223
H	0.609607	4.643169	0.918460
C	-3.600171	-0.465097	-1.360835
H	-3.818664	0.386498	-0.705568
C	-4.856755	-1.352324	-1.391213
H	-5.696837	-0.783264	-1.815251
H	-4.721249	-2.237914	-2.022373
H	-5.165144	-1.687177	-0.398379
C	-3.336079	0.094777	-2.768226
H	-2.514670	0.812989	-2.770922
H	-3.074901	-0.692800	-3.482940
H	-4.238250	0.598744	-3.144895
C	-2.164248	-3.032605	-0.937100
H	-3.175438	-3.327797	-0.624004
C	-2.015290	-3.349313	-2.432472
H	-1.064979	-2.981618	-2.829855
H	-2.050664	-4.435782	-2.597420
H	-2.811733	-2.898667	-3.033287
C	-1.166001	-3.836355	-0.091830
H	-0.134857	-3.534498	-0.294319
H	-1.339161	-3.693008	0.978340
H	-1.255566	-4.909251	-0.314800
C	2.941430	-1.855243	-1.971805
H	3.875497	-2.262806	-1.566573
C	2.006560	-3.042084	-2.225924
H	1.805822	-3.600600	-1.307122
H	1.053148	-2.711166	-2.645081
H	2.465909	-3.733663	-2.946853
C	3.264022	-1.135513	-3.293215
H	3.696155	-1.847223	-4.011233
H	2.360094	-0.717686	-3.744428
H	3.986867	-0.322954	-3.164202
C	3.819444	0.460128	-0.480331
H	3.786954	1.113406	-1.360873
C	5.171771	-0.275436	-0.481575
H	5.980454	0.458215	-0.354597
H	5.240838	-0.978217	0.356173
H	5.375119	-0.821963	-1.406464
C	3.753062	1.343275	0.770129
H	2.857210	1.960188	0.801420
H	3.762789	0.735084	1.680500
H	4.629404	2.006494	0.800331
C	-2.155273	2.970845	-0.358920
H	-2.718959	2.594618	-1.223235
C	-2.853592	2.481615	0.916782
H	-2.845584	1.396629	1.010828
H	-2.360633	2.884238	1.808511
H	-3.899283	2.821772	0.929420
C	-2.218790	4.508233	-0.383712
H	-3.259864	4.834592	-0.244426
H	-1.635243	4.941657	0.436846
H	-1.865882	4.946278	-1.321656
C	0.359568	3.427499	-1.737250
H	0.222488	4.428872	-1.309438
C	-0.344824	3.375511	-3.104468
H	0.082867	4.127484	-3.783384
H	-0.216981	2.393633	-3.570867
H	-1.420229	3.571294	-3.033735
C	1.863599	3.204124	-1.921223
H	2.404815	3.283762	-0.974338
H	2.058574	2.213135	-2.343688
H	2.277793	3.952390	-2.612669

Total Energy [a.u.]: -3826.4746451

Optimized Coordinates [Å] for (TPB)Fe(NNSiMe$_3$)

Atom	X	Y	Z
Fe	-0.460313	-0.117903	0.085474
P	0.396416	-0.700408	2.255089
P	-0.327116	2.260933	-0.568568
C	-1.851544	2.836216	-1.529546
C	-1.957038	4.306058	-1.975570
C	-2.104255	1.908899	-2.725480
P	0.257830	-1.867892	-1.427066
N	-2.200675	-0.138788	0.309997
Si	-4.994360	-0.398690	0.205352
C	-5.220142	-0.598636	-1.661313
C	-6.129317	0.948025	0.872034
C	-5.347123	-2.038963	1.075883
C	2.296932	1.005193	1.250758
C	2.075596	1.324040	-1.421872
C	1.152339	2.375467	-1.647261
C	3.990734	-1.287879	0.030333
C	3.195899	1.272797	-2.275374

C	2.654371	-1.100611	-0.376369
C	1.713627	0.571408	2.466867
C	2.015915	-2.196671	-0.999251
C	3.407146	2.217442	-3.281393
C	1.323353	-2.312138	2.643946
C	-1.354359	0.970804	3.727059
C	1.378549	3.344489	-2.636170
B	1.899607	0.317839	-0.163809
C	3.284835	2.006301	1.342769
C	3.682245	2.548875	2.566825
C	2.686963	-3.414185	-1.188393
C	2.502558	3.264879	-3.459273
C	-0.124482	3.515836	0.839526
C	2.116375	1.109643	3.697576
C	3.097575	2.101458	3.752061
C	-0.746979	-0.439215	3.736699
C	4.662095	-2.497302	-0.157461
C	0.281984	-1.278623	-3.234041
C	0.689680	4.771955	0.496831
C	4.007392	-3.569292	-0.764993
C	1.367006	-1.883000	-4.136886
C	1.974042	-2.377310	4.032685
C	-1.873771	-1.484775	3.791657
C	0.496973	-3.578954	2.367537
C	-0.569237	-3.582472	-1.375965
C	-1.103502	-1.358108	-3.898347
C	-1.473644	3.863872	1.492942
C	-2.062857	-3.474950	-1.026919
C	-0.383775	-4.535065	-2.572685
N	-3.359289	0.139137	0.588093
H	0.682333	4.163833	-2.775929
H	2.663894	4.009857	-4.234404
H	4.282351	2.140011	-3.923006
H	3.922161	0.474818	-2.142529
H	4.509041	-0.470275	0.526102
H	5.690613	-2.606774	0.179761
H	4.515411	-4.520326	-0.904735
H	2.186734	-4.258802	-1.649905
H	3.751185	2.370602	0.430093
H	4.445556	3.323626	2.595252
H	3.394955	2.522841	4.709139
H	1.656113	0.773606	4.623199
H	-0.132959	-0.547581	4.640576
H	-2.451482	-1.487942	2.861459
H	-1.502519	-2.496846	3.968304
H	-2.562840	-1.241028	4.610819
H	-2.046969	1.083140	2.887875
H	-1.922602	1.135685	4.651893
H	-0.593479	1.752790	3.656831
H	2.125224	-2.275714	1.899783
H	-0.135517	-3.470259	1.482807
H	1.166899	-4.431802	2.202171
H	-0.151696	-3.836977	3.210925
H	2.629726	-1.522136	4.219714
H	1.226008	-2.420979	4.833737
H	2.584755	-3.286329	4.111926
H	-1.290827	1.967834	-3.457593
H	-2.202115	0.870368	-2.404214
H	-3.033287	2.195051	-3.235439
H	-2.648502	2.648763	-0.797163
H	-2.984316	4.505652	-2.308505
H	-1.726513	5.020395	-1.182844
H	-1.302532	4.519740	-2.825836
H	0.459334	2.946316	1.569621
H	-2.063598	4.551971	0.879174
H	-2.084124	2.976507	1.682935
H	-1.296750	4.358551	2.456015
H	0.192873	5.406380	-0.244859
H	0.827953	5.373161	1.404951
H	1.680214	4.515210	0.112712
H	-0.061963	-4.039009	-0.517640
H	-2.631308	-3.016047	-1.843962
H	-2.481511	-4.475700	-0.856911
H	-2.226989	-2.873777	-0.128635
H	-0.965997	-4.215229	-3.441223
H	0.655682	-4.638309	-2.891492
H	-0.744459	-5.534516	-2.295552
H	0.527222	-0.217716	-3.104197
H	-1.128844	-0.711281	-4.784091
H	-1.334651	-2.373079	-4.234655
H	-1.908616	-1.035490	-3.232142
H	1.364924	-1.365707	-5.105459
H	2.363128	-1.772090	-3.701017
H	1.196985	-2.946551	-4.333618
H	-4.685631	-2.834957	0.715754
H	-5.207049	-1.951524	2.159230
H	-6.381824	-2.359068	0.897155
H	-7.183203	0.686867	0.715350
H	-5.977075	1.094351	1.947369
H	-5.945075	1.907684	0.375880
H	-5.027430	0.340520	-2.191812
H	-4.540590	-1.357458	-2.065776
H	-6.245434	-0.911901	-1.896587

Total Energy [a.u.]: -4235.6978066

Optimized Coordinates [Å] for [(TPB)Fe(NNSiMe$_3$)]Na(THF)

Atom	X	Y	Z
Fe	-0.491258	-0.902431	-0.092055
P	-2.536723	-1.808722	-0.482827
P	0.472805	3.508629	-0.182629
P	-0.395384	-0.056914	2.001439
Si	2.360995	-4.225951	-0.242108
H 1	2.589448	-0.316955	-0.460454
N	0.805765	-1.930660	-0.086140
O	4.847250	0.184754	-0.370432
C	-0.453973	0.945475	-1.135031
C	-3.769370	-2.259877	0.900658
H	-3.146575	-2.752043	1.659649
C	-2.143574	1.773966	0.939282
C	-1.525939	1.390125	2.154166
C	1.319682	0.702613	2.385251
H	1.548456	1.221592	1.444971
C	-4.857673	1.305234	-2.957003
H	-5.365732	2.085824	-3.519265
C	-3.528224	-0.677345	-1.531140
C	-4.383144	-0.990439	1.511069

H	-5.069815	-0.516949	0.801887
H	-3.633298	-0.248608	1.786667
H	-4.956839	-1.247922	2.410705
C	-3.107402	0.658701	-1.368448
N	1.924912	-2.514111	-0.125135
C	0.663463	1.902819	-1.129272
C	-3.800804	1.636410	-2.107629
H	-3.494618	2.678547	-2.045620
C	-3.094563	2.812566	1.016536
H	-3.631587	3.108210	0.120340
C	1.643119	-5.280792	1.158172
H	1.974618	-4.912418	2.135972
H	1.979360	-6.321633	1.063782
H	0.548488	-5.285022	1.159986
C	-5.252373	-0.026770	-3.103531
H	-6.068974	-0.288493	-3.772026
C	-1.767800	-3.278960	-2.811384
H	-0.718098	-3.004021	-2.670660
H	-2.238149	-2.519350	-3.443741
H	-1.798820	-4.232650	-3.354994
C	2.402992	-0.361608	2.641837
H	3.396212	0.109056	2.621706
H	2.391991	-1.183302	1.918690
H	2.288837	-0.808086	3.636231
C	-4.581083	-1.020605	-2.391850
H	-4.877088	-2.059255	-2.518864
C	5.770896	-0.408924	0.572431
H	5.385394	-1.394265	0.847175
H	5.814394	0.219536	1.472156
C	-0.690788	4.396272	-1.408917
H	-1.439474	3.615225	-1.586770
C	-1.809318	2.060670	3.354237
H	-1.323278	1.760630	4.277924
C	-2.487185	-3.425266	-1.463624
H	-3.529992	-3.694611	-1.670736
C	2.140669	4.391663	-0.407336
H	2.452288	4.380122	-1.459873
C	-3.386304	3.470665	2.210158
H	-4.130115	4.264496	2.224009
C	0.832395	-0.345419	-2.876469
H	0.866585	-1.165755	-3.591779
C	-1.852841	-4.545287	-0.628029
H	-1.822373	-5.482244	-1.199525
H	-2.400888	-4.742046	0.299657
H	-0.827846	-4.278627	-0.356671
C	-0.348361	-0.173526	-2.079684
H	-1.251670	-0.527212	-2.565445
B	-1.834321	0.980597	-0.420324
C	3.225958	3.707821	0.443531
H	4.178737	4.247422	0.349918
H	3.403920	2.667870	0.152325
H	2.947890	3.714134	1.504290
C	2.019397	5.862307	0.031713
H	1.604873	5.944149	1.043856
H	1.384433	6.446355	-0.639146
H	3.010397	6.335411	0.040006
C	1.378406	1.764818	3.492320
H	1.086737	1.357265	4.468569
H	0.741407	2.621963	3.267993
H	2.410364	2.128602	3.593955
C	-2.734097	3.103016	3.388260
H	-2.958793	3.604652	4.326237
C	-4.906440	-3.220238	0.511419
H	-5.562297	-3.374460	1.378319
H	-4.556747	-4.205420	0.191018
H	-5.524972	-2.797513	-0.288441
C	7.052203	0.820975	-1.007045
H	7.729223	0.799710	-1.865824
H	7.296186	1.703111	-0.403858
C	4.246115	-4.223031	-0.082550
H	4.704574	-3.593807	-0.855543
H	4.657252	-5.234351	-0.189653
H	4.559881	-3.840465	0.896552
C	1.902189	-4.960344	-1.926020
H	0.819725	-4.984646	-2.085632
H	2.276568	-5.988513	-2.015515
H	2.345019	-4.373086	-2.739418
C	1.760660	1.692512	-1.947672
H	2.541911	2.442605	-2.021332
C	1.872844	0.543264	-2.804573
H	2.743031	0.440952	-3.451483
C	-1.418578	5.585178	-0.759425
H	-0.749330	6.432654	-0.577131
H	-1.869910	5.301355	0.195937
H	-2.218663	5.943074	-1.421649
C	-0.628951	-1.122784	3.571916
H	0.020070	-0.669532	4.333872
C	-0.079628	4.766935	-2.766297
H	-0.862035	5.127462	-3.447700
H	0.402921	3.906257	-3.240526
H	0.662778	5.569122	-2.676676
C	-0.136887	-2.557222	3.310982
H	-0.158914	-3.136245	4.243898
H	0.878358	-2.596754	2.911411
H	-0.785456	-3.059670	2.585488
C	-2.049101	-1.179469	4.152338
H	-2.734125	-1.695637	3.476336
H	-2.469147	-0.194061	4.361233
H	-2.030828	-1.746333	5.092684
C	7.118530	-0.449775	-0.146096
H	7.186520	-1.341845	-0.779730
H	7.962992	-0.459178	0.549093
C	5.580192	0.850132	-1.428981
H	5.180636	1.861890	-1.543545
H	5.414804	0.298572	-2.363139

Total Energy [a.u.]: -4630.4797417

Optimized Coordinates [Å] for (TPB^{Me})Fe(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 5-Me).

Atom	X	Y	Z
Fe	-0.344283	0.163942	-0.070870
P	0.132148	-1.018190	1.710495
P	0.575540	2.140022	0.255173
P	0.400390	-0.481206	-2.055473
C	2.986577	1.168380	-0.548822
C	2.273524	2.374083	-0.401885
C	3.371082	-0.904770	4.316727

C	0.894263	0.780040	-3.331571
C	3.912708	-3.440814	-1.638814
C	1.774764	-0.844158	2.497710
C	2.072308	-1.093940	3.843573
C	-0.889756	-1.370536	-3.048348
C	2.829901	3.599254	-0.789434
C	-0.362094	3.534823	-0.538948
C	2.760514	-0.414354	1.593408
C	1.794493	-1.676480	-2.021873
C	3.690816	-2.400591	-0.730945
C	4.263650	1.239016	-1.135725
C	2.019095	-2.705682	-2.940878
C	4.060622	-0.222550	2.097990
C	-0.026494	-2.859042	1.507166
C	-1.033172	-0.713140	3.124921
C	2.633594	-1.491063	-0.904572
C	4.364676	-0.465657	3.438800
C	4.818334	2.457318	-1.534193
C	4.105413	3.644111	-1.354679
C	3.081516	-3.593354	-2.748811
B	2.413082	-0.212679	0.037920
C	0.688333	2.780228	1.996599
H	3.603198	-1.086313	5.363260
H	1.709142	1.402355	-2.958553
H	4.731984	-4.137392	-1.474811
H	1.296665	-1.423190	4.530801
H	-0.544736	-1.584737	-4.066312
H	2.270417	4.524033	-0.670346
H	-0.365842	3.398151	-1.624420
H	4.345766	-2.301437	0.131907
H	4.828666	0.322881	-1.294269
H	1.362286	-2.838058	-3.797242
H	4.844281	0.139241	1.436147
H	0.699239	-3.192156	0.759952
H	-2.062588	-0.769872	2.764010
H	5.376490	-0.302137	3.803078
H	5.804960	2.480365	-1.991648
H	4.531512	4.594697	-1.665811
H	3.247680	-4.405265	-3.452628
H	1.291913	2.091572	2.593751
N	-1.971756	0.100518	-0.106545
N	-3.317678	0.013691	-0.069507
Si	-4.305418	1.510556	-0.019599
Si	-4.278929	-1.500883	-0.019483
C	-5.964574	-0.727527	-0.430284
H	-6.054829	-0.668718	-1.523737
H	-6.806919	-1.341991	-0.085813
C	-6.015509	0.702738	0.179678
H	-6.817841	1.303422	-0.268844
H	-6.245285	0.639762	1.252096
C	-3.843901	2.585042	1.461939
H	-4.049948	2.059059	2.401295
H	-2.779655	2.842446	1.456363
H	-4.415894	3.521339	1.468204
C	-3.732880	-2.794864	-1.274445
H	-3.727495	-2.399905	-2.295087
H	-2.729781	-3.175196	-1.053625
H	-4.422371	-3.648463	-1.245201
C	-4.294813	-2.301164	1.695488
H	-4.988757	-3.151985	1.705709
H	-3.308739	-2.681254	1.983631
H	-4.620993	-1.598326	2.470806
C	-4.134607	2.477209	-1.632333
H	-4.679703	3.428453	-1.588916
H	-3.084594	2.702090	-1.848125
H	-4.531248	1.901693	-2.476939
H	-0.863081	0.295877	3.512641
H	-0.903752	-1.432625	3.941703
H	0.164140	-3.383447	2.450548
H	-1.030559	-3.111767	1.151298
H	-1.155937	-2.309890	-2.559280
H	-1.785510	-0.745440	-3.104490
H	0.030907	1.420485	-3.545303
H	1.211635	0.294507	-4.261494
H	-1.396526	3.525528	-0.187290
H	0.073266	4.513152	-0.306994
H	1.144972	3.775855	2.031571
H	-0.315173	2.833876	2.433374

Total Energy [a.u.]: -4172.0373082

Optimized Coordinates [Å] for (TPB)Fe(CO)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 6).

Atom	X	Y	Z
Fe	1.621516	0.519055	0.518515
P	-0.005247	0.170353	2.081717
P	1.295430	2.459467	-0.669267
Si	4.866007	-1.851346	0.447344
Si	3.017898	-2.999963	-1.644858
N	2.364191	-0.769991	-0.154031
N	3.300455	-1.704426	-0.431773
C	-0.129391	2.753189	-1.837515
C	-1.642109	1.059418	1.943081
C	2.740333	1.308869	1.538605
O	3.603603	1.767259	2.192213
C	-0.067220	3.776695	-2.802110
H	0.801089	4.423068	-2.854751
C	-0.632604	-1.625629	2.155060
H	-1.274935	-1.667779	1.267237
C	-2.157000	1.321076	0.650654
C	-2.899462	-1.602050	-1.124502
C	-2.332637	1.544468	3.064622
H	-1.969977	1.331054	4.063307
C	0.491354	0.533422	3.877055
H	-0.363891	0.229478	4.491599
C	-1.254969	1.901617	-1.812594
C	-3.286314	2.159652	0.552188
H	-3.660945	2.432146	-0.430946
C	-0.953003	-0.961643	-2.428198
H	-0.165820	-0.249269	-2.651787
C	-1.091114	3.982929	-3.724458
H	-1.012765	4.787211	-4.451449
C	2.744147	2.674043	-1.871210
H	2.593865	3.639320	-2.366742
C	-1.852510	-0.657046	-1.376292
P	-4.221091	-1.291749	0.171737
C	-5.013836	-3.000260	0.407896
H	-5.330912	-3.422485	-0.553733

C	-4.010798	-3.962247	1.067174
H	-3.094995	-4.084570	0.481126
H	-4.464564	-4.953971	1.192804
H	-3.726784	-3.600500	2.061549
C	-6.265189	-2.879178	1.296420
H	-6.040367	-2.359974	2.235769
H	-6.640233	-3.878962	1.550828
C	-5.474893	-0.347297	-0.923298
H	-4.832972	0.412857	-1.388479
C	-6.518765	0.403577	-0.079090
H	-6.046884	0.980319	0.721550
H	-7.242643	-0.277466	0.380081
H	-7.086409	1.097737	-0.713132
C	-6.135745	-1.151225	-2.050437
H	-5.397014	-1.647693	-2.687651
H	-6.733792	-0.487220	-2.689022
H	-6.815598	-1.916176	-1.657246
C	0.760593	2.024804	4.141849
H	0.946221	2.173751	5.213698
H	-0.079457	2.663808	3.859856
H	1.647622	2.369973	3.607361
C	1.364479	4.057032	0.357457
H	2.132099	3.825133	1.105363
C	-2.254928	2.098476	-2.791761
H	-3.101632	1.416765	-2.826761
C	-1.505772	-1.935728	3.379985
H	-1.933475	-2.940382	3.276426
H	-2.337056	-1.232682	3.486226
H	-0.923055	-1.933255	4.308182
C	-2.194726	3.132774	-3.722183
H	-2.991561	3.258444	-4.450964
C	0.458532	-2.689361	1.977412
H	1.081803	-2.795823	2.871132
H	1.111679	-2.455000	1.136437
H	-0.012076	-3.663688	1.791796
B	-1.619325	0.783753	-0.742305
C	-1.024695	-2.124978	-3.185441
H	-0.301453	-2.309243	-3.975097
C	0.030789	4.265790	1.088675
H	0.124474	5.083771	1.813997
H	-0.286775	3.370208	1.624714
H	-0.766416	4.531506	0.385698
C	2.740481	1.580941	-2.948446
H	3.575922	1.737242	-3.643171
H	1.814894	1.586009	-3.533509
H	2.856667	0.592327	-2.494465
C	1.694723	-0.302543	4.343295
H	2.592457	-0.075963	3.763150
H	1.508247	-1.377309	4.284805
H	1.913908	-0.063210	5.391907
C	5.674474	-3.137561	-0.693811
H	6.191774	-2.591041	-1.494537
H	6.445498	-3.728227	-0.181058
C	1.777131	5.356281	-0.351787
H	1.018421	5.684158	-1.069850
H	2.736524	5.280019	-0.871767
H	1.875871	6.153985	0.395863
C	1.457268	-4.001227	-1.309757
H	1.524704	-4.521317	-0.348193
H	1.326249	-4.760389	-2.092289
H	0.557981	-3.379701	-1.298830
C	4.099819	2.719934	-1.153963
H	4.343097	1.747367	-0.722543
H	4.132812	3.457862	-0.346514
H	4.887701	2.975718	-1.874371
C	-2.961632	-2.766467	-1.912993
H	-3.756747	-3.484673	-1.751244
C	4.587384	-2.496017	2.200323
H	3.947674	-1.814691	2.771402
H	5.538699	-2.589394	2.739310
H	4.104707	-3.480106	2.194614
C	-2.043350	-3.037542	-2.924755
H	-2.136230	-3.949063	-3.510331
C	4.570688	-4.043217	-1.303081
H	4.293998	-4.825120	-0.582540
H	4.926375	-4.569088	-2.199402
C	5.889468	-0.272356	0.504580
H	6.061867	0.131067	-0.499161
H	6.870550	-0.504615	0.940584
H	5.431609	0.507937	1.118291
C	2.978087	-2.302199	-3.400724
H	2.163644	-1.580255	-3.523996
H	2.827815	-3.105114	-4.133950
H	3.914953	-1.791139	-3.650123
C	-3.478493	2.331453	2.941984
H	-3.979571	2.702188	3.832445
C	-3.943262	2.663752	1.673836
H	-4.804877	3.315520	1.552264
H	-7.078792	-2.342022	0.801213

Total Energy [a.u.]: -4757.0880603

Optimized Coordinates [Å] for (TPB)Fe(CN^{t}Bu)(NR) (R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl, 7).

Atom	X	Y	Z
Fe	1.409126	-0.176523	-0.086693
P	0.027114	-0.608279	-1.839581
P	1.322816	-1.806068	1.515956
Si	3.773804	3.122692	-0.105591
Si	1.220583	3.975919	1.225036
N	1.652167	1.386753	0.316217
N	2.152927	2.644446	0.474332
C	-0.184996	-2.191287	2.549251
C	-1.439373	-1.749730	-1.622744
C	2.913678	-0.858652	-0.755152
C	-0.073299	-2.980415	3.710703
H	0.888069	-3.388876	3.998967
C	-0.889173	0.933930	-2.480990
H	-1.628416	1.094129	-1.686207
C	-2.100130	-1.770894	-0.371509
C	-3.632555	1.219875	0.611720
C	-1.866327	-2.626559	-2.633655
H	-1.395147	-2.605059	-3.609177
C	0.820589	-1.308740	-3.416247
H	0.026872	-1.381626	-4.168220
C	-1.438948	-1.639462	2.214512
C	-3.096314	-2.750887	-0.174182
H	-3.574109	-2.833644	0.798188

C	-1.926605	1.223266	2.336330
H	-1.064821	0.760969	2.805137
C	-1.166448	-3.245672	4.531916
H	-1.043767	-3.864198	5.417451
C	2.524140	-1.373393	2.920139
H	2.483877	-2.204407	3.633207
C	-2.491633	0.585090	1.202296
P	-4.525756	0.501467	-0.875397
C	-5.444494	2.004973	-1.587645
H	-6.092692	2.462644	-0.830026
C	-4.444670	3.063137	-2.083772
H	-3.788077	3.428847	-1.289189
H	-4.983288	3.924997	-2.499147
H	-3.811787	2.655952	-2.879941
C	-6.341719	1.558016	-2.756064
H	-5.768976	1.004884	-3.509926
H	-6.780018	2.435909	-3.248430
C	-5.891758	-0.480903	0.038042
H	-5.302665	-1.048716	0.770336
C	-6.566109	-1.506565	-0.889246
H	-5.827597	-2.098053	-1.437643
H	-7.224585	-1.026720	-1.621045
H	-7.187142	-2.194889	-0.300264
C	-6.931758	0.339557	0.811635
H	-6.465524	1.032393	1.518960
H	-7.588464	-0.328309	1.385382
H	-7.573791	0.919538	0.138019
C	1.391484	-2.717325	-3.193855
H	1.854536	-3.081742	-4.121039
H	0.622299	-3.437131	-2.904010
H	2.155564	-2.715286	-2.414383
C	1.902869	-3.531473	0.961892
H	2.695153	-3.285157	0.244769
C	-2.522092	-1.881589	3.091837
H	-3.484171	-1.419314	2.883103
C	-1.654697	0.711658	-3.793869
H	-2.253124	1.601647	-4.025308
H	-2.339461	-0.138743	-3.736289
H	-0.975854	0.560075	-4.641305
C	-2.404504	-2.687052	4.220772
H	-3.266088	-2.858003	4.861514
C	-0.024606	2.199228	-2.562783
H	0.668612	2.171362	-3.409501
H	0.557695	2.345655	-1.652824
H	-0.674086	3.072816	-2.705963
B	-1.854091	-0.845419	0.897859
C	-2.419146	2.401221	2.884404
H	-1.940391	2.841116	3.754836
C	0.765898	-4.228048	0.198938
H	1.143858	-5.121782	-0.314184
H	0.312698	-3.571652	-0.546351
H	-0.027264	-4.546669	0.884303
C	2.079081	-0.098663	3.650821
H	2.779106	0.131180	4.464890
H	1.082178	-0.208099	4.090289
H	2.061878	0.752949	2.963661
C	1.891487	-0.370468	-3.995876
H	2.645032	-0.105389	-3.250569
H	1.460930	0.555384	-4.384450
H	2.401797	-0.867968	-4.831768
C	3.837809	4.863221	0.656075
H	4.285027	4.775118	1.655957
H	4.485259	5.548362	0.092164
C	2.496747	-4.494111	2.002552
H	1.734369	-4.861119	2.696954
H	3.310687	-4.054225	2.586536
H	2.904740	-5.373500	1.486156
C	-0.478296	4.209925	0.445570
H	-0.382559	4.561218	-0.587392
H	-1.059148	4.954349	1.004108
H	-1.053695	3.280161	0.437518
C	3.973331	-1.236908	2.440867
H	4.082408	-0.380238	1.773192
H	4.324519	-2.124525	1.906304
H	4.635564	-1.081359	3.302885
C	-4.122487	2.406685	1.190789
H	-4.996070	2.888855	0.767989
C	3.854273	3.138928	-1.993879
H	3.599457	2.155127	-2.402882
H	4.859342	3.401543	-2.348325
H	3.148952	3.864624	-2.414796
C	-3.538155	2.996171	2.308720
H	-3.960478	3.908040	2.724359
C	2.388594	5.410081	0.775553
H	2.064811	5.814919	-0.193179
H	2.328322	6.242948	1.489224
C	5.151102	2.029358	0.575446
H	5.141261	2.013281	1.670897
H	6.131676	2.403280	0.252467
H	5.046477	1.000363	0.221015
C	1.083146	3.747637	3.097465
H	0.599701	2.797903	3.347475
H	0.494516	4.554932	3.551903
H	2.073959	3.749557	3.566887
C	-2.881163	-3.560498	-2.425761
H	-3.172824	-4.233212	-3.228346
C	-3.486229	-3.638118	-1.175687
H	-4.249865	-4.385100	-0.973324
H	-7.168192	0.921037	-2.428494
N	4.002414	-1.172610	-1.133031
C	5.269176	-1.579182	-1.682635
C	5.790639	-0.470268	-2.619895
C	6.270372	-1.807324	-0.531510
C	5.089321	-2.890556	-2.474137
H	5.090160	-0.296357	-3.442204
H	5.925335	0.468858	-2.075522
H	6.756343	-0.765779	-3.045047
H	5.922015	-2.603484	0.133507
H	7.244099	-2.100237	-0.939629
H	6.402794	-0.897127	0.060322
H	6.057827	-3.222810	-2.864251
H	4.687503	-3.680520	-1.831250
H	4.407156	-2.749973	-3.316753

Total Energy [a.u.]: -4894.4260492